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Monsanto Research Corp., Dayton, Ohio

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16. ABSTRACT

The report summarizes the assessment of air emissions from the manufacture of carbon black, currently manufactured in the U.S. by two major processes: thermal and oil furnace. Sources of atmospheric emissions within oil furnace plants (about 90% of the 30 U.S. carbon black plants) include the main process vent, dryer vent, pneumatic system vent, oil feedstock storage tanks, vacuum cleanup system vent, and fugitive sources. To assess the severity of emissions from this industry, a representative plant was defined as using the oil furnace process and with a mean production rate of 50,000 metric tons/yr. For a representative plant, calculated source severities were: 0.02 for particulates emitted from the main process vent; 0.046 and 0.58 for SOx and NOx, respectively, from the dryer vent; 21 for HC emitted from the main process vent; and 27 for carbon black fugituve emissions. The average number of persons exposed to high contaminant levels from carbon black manufacture was estimated and designated as the 'affected population.' The calculation was made for each species emitted and for each emission point within a representative plant for which the source severity exceeds 0.1. The largest value obtained was 11,000 persons, due to H2S emissions from the main process vent. Assuming the same control levels in 1974 and 1980, emissions from the industry will increase by 14% by 1980.

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Sulfur Oxides		Fugitive Emissions	07B	
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SOURCE ASSESSMENT:
CARBON BLACK MANUFACTURE

by

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PREFACE

The Industrial Environmental Research Laboratory (IERL) of EPA has the responsibility for insuring that pollution control technology is available for stationary sources to meet the requirements of the Clean Air Act, the Federal Water Pollution Control Act, and solid waste legislation. If control technology is unavailable, inadequate, uneconomical, or socially unacceptable, then financial support is provided for the development of the needed control techniques for industrial processes and extractive process industries. Approaches considered include: process modifications, feedstock modifications, add-on control devices, and complete process substitution. The scale of the control technology programs ranges from bench- to full-scale demonstration plants.

The Chemical Processes Branch of the Industrial Processes Division of IERL has the responsibility for investing tax dollars in programs to develop control technology for a large number (>500) of operations in the chemical industries. As in any technical program, the first question to answer is, "Where are the unsolved problems?" This is a determination which should not be made on the basis of superficial information; consequently, each of the industries is being evaluated in detail to determine if there is, in EPA's judgment, sufficient environmental risk associated with the process to invest in the development of control technology. This report contains the data necessary to make that decision for the air emissions from carbon black manufacture.

Monsanto Research Corporation has contracted with EPA to investigate the environmental impact of various industries which represent sources of pollution in accordance with EPA's responsibility as outlined above. Dr. Robert C. Binning serves as Program Manager in this overall program entitled, "Source Assessment," which includes the investigation of sources in each of four categories: combustion, organic materials, inorganic materials, and open sources. Dr. Dale A. Denny of the Industrial Processes Division at Research Triangle Park serves as EPA Project Officer. In this study of carbon black manufacture, Mr. Edward J. Wooldridge and Dr. I. Atly Jefcoat served as EPA Task Officers.

Data on the combustion efficiency of carbon monoxide in the flare were supplied by Dr. William F. Herget, Environmental Sciences Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, N.C. These data were obtained in an effort independent of the present study using the ROSE (Remote Optical Sensing of Emissions) System.

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SYMBOLS

Symbol	Definition
A	Area, km^2
C	Diameter factor
C_1	Concentration of trace element in sample from front half (probe and filter) of sampling train, g/m^3
C_2	Concentration of trace element in sample from back half (impingers) of sampling train, g/m^3
Cap	Production capacity, metric tons/yr
C_i	Production capacity of plant i, metric tons/yr
C_p	Heat capacity at constant pressure of stack gas, kcal/g-°K
D	Tank diameter, ft
D'	Stack diameter, m
$\overline{D}_p$	Mean population density, persons/km^2
D_{p_i}	County population density for plant i, persons/km^2
e	Euler's constant $\cong$ 2.72
E	Emission factor, g/kg
E'	Emission factor, lb/ton
F	Hazard factor, g/m^3
F_g	Equivalent gasoline working loss, bbl/yr
F_p	Paint factor
H	Effective emission height, m
H'	Tank outage, ft
H_s	Physical stack height, m
K_T	Turnover factor
$K(\lambda, T)$	Spectral absorption coefficient of CO at wave length λ and temperature T, s^2/kg
L	Total petrochemical loss, bbl/yr
$\hat{L}$	Optical path length in plume from flare, m
L_1	Total petrochemical loss, lb/yr

SYMBOLS (continued)

Symbol	Definition
L_g	Total equivalent gasoline loss, bbl/yr
L_y	Equivalent gasoline breathing loss, bbl/yr
M	Molecular weight of material stored, g/g mole
M'	Molecular weight of stack gas, g/g mole
m	Value of right-hand side of equation 4
N	Number of turnovers per year
$N_{bb}(\lambda, T)$	Spectral radiance of a blackbody at wavelength λ and temperature T, W/cm^2-sr-μ
$N_s(\lambda, T)$	Spectral radiance of CO at wavelength λ and temperature T, W/cm^2-sr-μ
P	Vapor pressure, psia
P'	Atmospheric pressure, dyne/m^2
$\hat{P}$	Partial pressure of CO, Pa
Q	Mass emission rate, g/s
Q_H	Heat emission rate, kcal/s
R	Universal gas constant, dyne-m/g mole-°K
S	Source severity
t, t_0	Averaging times, min
T_a	Ambient air temperature, °K
T_s	Stack gas temperature, °K
$\overline{u}$	Average wind speed, m/s
v	Tank capacity, bbl
V_s	Stack gas exit velocity, m/s
W	Liquid density, lb/gal
x	Distance downwind from source, m
ΔH	Plume rise, m
ΔT	Average daily ambient temperature change, °F
ε_λ	Emissivity of CO at wavelength λ
σ_z	Vertical dispersion coefficient, m

SYMBOLS (continued)

Symbol	Definition
χ_{max}	Maximum mean ground level concentration (short-term average), g/m^3
$\bar{\chi}_{max}$	Maximum mean ground level concentration (long-term average), g/m^3
$\bar{\chi}(x)$	Annual mean ground level concentration as a function of distance, g/m^3

SECTION I

INTRODUCTION

Carbon black is a generic name for the class of finely divided carbons produced by the thermal decomposition of hydrocarbons. The principal uses of carbon black are as a reinforcing agent in rubber compounds (especially tires) and as a black pigment in inks, coatings, paper, and plastics. Two major processes are presently used in the United States to manufacture carbon black: the oil furnace process and the thermal process.

Two other processes, the lamp process for the production of lampblack and the cracking of acetylene to produce acetylene black, are used at one plant each in the United States. However, these are small volume, specialty black operations which constitute less than 1% of total U.S. carbon black production. (Personal communication with H. J. Collyer, Cabot Corporation, Billerica, Massachusetts, 11 May 1977.) Two additional processes, the channel process and the gas furnace process, were formerly operated in the country. The gas furnace process was phased out in the 1960's, and the last channel black plant was closed in 1976. (Personal communication with H. J. Collyer, Cabot Corporation, Billerica, Massachusetts, 11 May 1977.)

In the thermal process, natural gas is injected into a heated refractory chamber where it decomposes to form carbon black. Since the decomposition reaction is endothermic, the chamber is alternately heated (by burning natural gas) and injected with feed gas in a cyclic process. By contrast, in the oil furnace process, a liquid hydrocarbon feedstock is injected continuously into the combustion zone of a natural gas fired furnace where it is decomposed to form carbon black. In the channel process, which is still used in some foreign countries, thousands of small natural gas flames impinge on channel irons and deposit carbon black which is subsequently removed by mechanical scraping. Acetylene black is made in a continuous process by the exothermic decomposition of acetylene in water-cooled retorts lined with firebrick. Lampblack is made in a semicontinuous or batch operation by burning liquid hydrocarbons in shallow, open pans in a restricted area with a limited air supply. The gas furnace process was similar to the oil furnace process except that natural gas was used instead of the liquid hydrocarbon feedstock.

Although the manufacture of lampblack dates from antiquity, modern carbon black production originated in the 1870's with the development of the channel process. Production was confined to the United States, where large quantities of inexpensive natural gas were available. In 1912, the serendipitous discovery of carbon black's unique reinforcement properties in rubber tires led to a transformation of the industry from small-scale pigment production to bulk chemical manufacture which today is carried out on a worldwide basis. The gas furnace process was introduced in 1922, and the oil furnace process in 1943. The versatility and high yields obtainable with the latter process have resulted in its predominance in the industry today. As illustrated in Figure 1,[1] the oil

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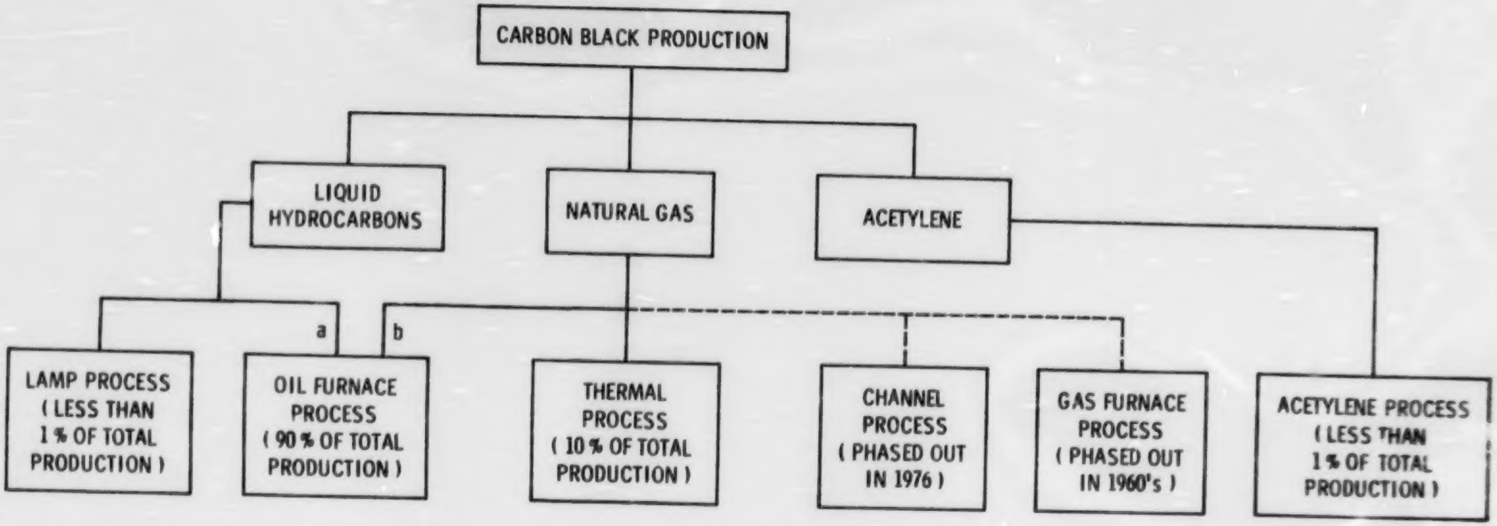
[1] Carbon Black. In: Minerals Yearbook, Vol. 1. Metals, Minerals, and Fuels. U.S. Government Printing Office, Washington, D.C. 1940-1974.


CARBON BLACK PRODUCTION
LIQUID HYDROCARBONS
NATURAL GAS
ACETYLENE
a
b
LAMP PROCESS (LESS THAN 1 % OF TOTAL PRODUCTION)
OIL FURNACE PROCESS (90 % OF TOTAL PRODUCTION)
THERMAL PROCESS (10 % OF TOTAL PRODUCTION)
CHANNEL PROCESS (PHASED OUT IN 1976)
GAS FURNACE PROCESS (PHASED OUT IN 1960's)
ACETYLENE PROCESS (LESS THAN 1 % OF TOTAL PRODUCTION)

a. LIQUID HYDROCARBONS ARE USED AS THE FEEDSTOCK FOR CARBON BLACK PRODUCTION
b. NATURAL GAS IS USED AS A FUEL IN THE PROCESS

Figure 1. Schematic breakdown of U.S. carbon black production[1]

furnace process accounts for approximately 90% of total carbon black production in the United States. For this reason, the oil furnace process is the primary subject of the present study.

This document presents a detailed study of the carbon black industry from the standpoint of atmospheric emissions and their potential environmental impact. The major results of the study, summarized in Section II, include emission factors for each species emitted to the atmosphere from each emission point within a representative carbon black plant. Also tabulated are several factors designed to measure the environmental hazard potential of carbon black operations. These consist of source severities, the industry contribution to total atmospheric emissions of criteria pollutants, and the number of persons exposed to high contaminant levels from a representative plant.

The report includes detailed descriptions of the oil furnace process (Section III), the emission points within a plant and the materials emitted to the atmosphere (Section IV), and present and future aspects of pollution control technology in the industry (Section V). Economic and production trends in carbon black manufacture, as well as in those industries that are major consumers of carbon black, are analyzed in Section VI. On the basis of this analysis, an estimate of carbon black production through the remainder of the present decade is given.

SECTION II

SUMMARY

Carbon black is currently manufactured in the U.S. by two major processes: the thermal process and the oil furnace process. The oil furnace process is the predominant method of production, accounting for about 90% of the carbon black produced domestically. The 30 carbon black plants currently in operation in the U.S. have a combined capacity of 1.88×10^6 metric tons/yr (2.1×10^6 tons/yr).[a] Carbon black plant capacities range in size from 22.6×10^3 to 174.2×10^3 metric tons/yr and typically operate at ∿80% of capacity.

Sources of atmospheric emissions within oil furnace carbon black plants include the main process vent, the dryer vent, the pneumatic system vent, the oil feedstock storage tanks, the vacuum cleanup system vent, and fugitive sources.

In the oil furnace process, carbon black is produced by the thermal decomposition of a liquid hydrocarbon feedstock in a refractory-lined steel furnace. The heat required to carry out the decomposition reaction is supplied by burning natural gas. The carbon black is recovered from the reactor exhaust gases by means of bag filters, and the gaseous reaction products, together with residual carbon black, are vented to the atmosphere through the main process vent.

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[a] 1 metric ton = 10 grams = 2205 pounds = 1.1 short tons; (short tons are designated "tons" in this document); other conversion factors and metric system prefixes are presented in Section IX.

The recovered carbon black is mixed with water and pelletized. The pellets are subsequently dried in a gas-fired dryer. A part of the combustion gases is fed directly to the interior of the dryer, and the carbon black thus entrained in the gas stream is subsequently removed using either a bag filter or wet scrubber. The combustion gases are then vented to the atmosphere through the dryer vent.

Carbon black recovered from the reactor effluent stream is transported from the bag filters to the product finishing (pelleting, drying, packaging, and storage) area of the plant by a pneumatic conveying system. The black is recovered from the entraining air stream by a bag filter, and the filtered air is exhausted through the pneumatic system vent.

The oil feedstock storage tanks are subject to working and breathing losses which are uncontrolled in all carbon black plants. However, these storage tanks meet EPA New Source Performance Standards for this type of emission point.

Plantwide vacuum cleanup systems are used to pick up fugitive carbon black from leaks and spills. They are also used in some plants to control emissions from carbon black storage bins and the packaging operation. The exhaust stream from the vacuum system is passed through a bag filter to remove the carbon black and then vented to the atmosphere.

The small particle size and light, fluffy character of carbon black give rise to numerous sources of fugitive emissions within the plant. These are: (1) leaks in the pneumatic system, storage bins, bagging system, and other process equipment; (2) cleaning of plugged process equipment; (3) spillage from torn and broken bags; (4) spillage during the loading of hopper cars and Sealdbins® (collapsible rubber containers); (5) cleaning and sweeping the bottoms of hopper cars; and (6) dismantling of process equipment for repairs.

Emission factors for a carbon black plant employing the oil furnace process were computed from field sampling data obtained in this study for the main process vent, and from emissions data available in the literature for the other emission points. The emission factors were used to generate a number of other factors designed to quantify the potential hazard from carbon black production. The source severity was defined as the ratio of the time-averaged maximum ground level concentration to a potentially hazardous concentration of a given pollutant from a given source. Using Gaussian plume dispersion theory, source severities were calculated for a representative carbon black plant which was defined as a plant using the oil furnace process, and having the industry mean production rate of 5.1×10^4 metric tons/yr (5.6×10^4 tons/yr). Results are summarized in Table 1. Also listed are the annual mass emissions from the entire U.S. carbon black industry, and the percentage contribution of the industry to the total mass emissions of criteria pollutants (particulate, NO_x, SO_x, carbon monoxide, and hydrocarbons) from all stationary sources.

The average number of persons exposed to high contaminant levels from carbon black production was estimated and designated as the "affected population." The calculation was made for each species emitted and for each emission point within a representative plant for which the source severity exceeds 0.1. The largest value obtained was 11,000 persons, due to hydrogen sulfide emissions from the main process vent.

Carbon black production in 1974 totaled 1.54×10^6 metric tons (1.69×10^6 tons). Production in 1980 is expected to total 1.76×10^6 metric tons (1.94×10^6 tons). Thus

Table 1. SOURCE SEVERITIES AND INDUSTRY CONTRIBUTION TO TOTAL EMISSIONS FOR CARBON BLACK PRODUCTION.

Material emitted	Emission factor, g/kg	Emissions from all plants		Source severity[b]	Industry contribution to total emissions,[a] %		
		metric tons/yr	tons/yr		Nationwide	Texas	Louisiana
Criteria pollutants							
Particulate matter[c]		1,011	1,116				
Main process vent	0.11 ± 70%	170	185	0.02	0.01	0.08	0.09
Dryer vent	0.12 ± 89%	185	203	0.034			
Pneumatic system vent	0.3 ± 93%	460	508	0.053			
Vacuum cleanup vent	0.03 ± 58%	46	50	0.008			
Fugitive emissions	0.1	150	170	1.2			
Sulfur oxides		353	390				
Main process vent	0.0[f]	0[f]	0[f]	0.0[f]	0.001	0.02	0.07
Dryer vent	0.23 ± 60%	353	390	0.046			
Nitrogen oxides		1,352	1,490				
Main process vent	0.28 ± 15%	430	474	0.16	0.008	0.04	0.12
Dryer vent	0.6 ± 200% - 100%	922	1,016	0.58			
Hydrocarbons[d]		78,007	85,909				
Main process vent	50 ± 48%	76,900	84,690	21	0.31	1.5	1.4
Oil storage tanks	0.72 ± 10%	1,107	1,219	0.84			
Carbon monoxide		2,153,000	2,371,000				
Main process vent	1,400 ± 19%	2,153,000	2,371,000	1.8	2.3	13	13
Hazardous materials							
Beryllium		<0.0034	<0.0037				
Main process vent	0.0000022 ± 16%	<0.0034	<0.0037	<0.028			
Mercury		0.23	0.25				
Main process vent	0.00015 + 386% - 100%	0.23	0.25	0.42			
Chemical substances							
Hydrogen sulfide		46,140	50,814				
Main process vent	30 ± 82%	46,140	50,814	20			
Carbon disulfide		46,140	50,814				
Main process vent	30 ± 76%	46,140	50,814	7.6			
Carbonyl sulfide		15,380	16,938				
Main process vent	10 ± 99%	15,380	16,938	2.1			
Carbon black		1,011	1,116				
Main process vent	0.11 ± 70%	170	185	0.45			
Dryer vent	0.12 ± 89%	185	203	0.76			
Pneumatic system vent	0.3 ± 93%	460	508	1.2			
Vacuum cleanup vent	0.03 ± 58%	46	50	0.34			
Fugitive emissions	0.1	150	170	27			
Methane[e]		38,450	42,350				
Main process vent	25 ± 47%	38,450	42,350	–[e]			
Acetylene[e]		69,200	76,200				
Main process vent	45 ± 48%	69,200	76,200	–[e]			
Ethylene[e]		2,460	2,712				
Main process vent	1.6 ± 85%	2,460	2,712	–[e]			
Ethane[e]		0[f]	0[f]				
Main process vent	0.0[f]	0[f]	0[f]	–[e,f]			
Propylene		0[f]	0[f]				
Main process vent	0.0[f]	0[f]	0[f]	–[e,f]			
Propane[e]		307	340				
Main process vent	0.0[f]	307	340	–[e f]			
Isobutane		153	169				
Main process vent	0.10 ± 80%	153	169	0.001			
n-Butane		414	457				
Main process vent	0.27 ± 57%	414	457	0.003			
n-Pentane		0[f]	0[f]				
Main process vent	0.0[f]	0[f]	0[f]	0.0[f]			
POM		3.1	3.4				
Main process vent	0.002 ± 52%	3.1	3.4	2.1			
Trace elements[g]		<400	<400				
Main process vent	<0.25 ± 43%	<400	<440	<2.7			

[a] Industry contribution calculated only for criteria pollutants.

[b] Calculated assuming no plume rise. If plume rise is included in the calculations, severities of emissions from the main process vent are reduced by 80%; severities of emissions from the dryer vent are reduced by 60%; severities of other emissions are unchanged.

[c] The particulate matter is carbon black. Source severities are based on the primary ambient air quality standard for particulate matter.

[d] Total nonmethane hydrocarbons. Source severities are based on the primary ambient air quality standard for hydrocarbons. The individual hydrocarbon species are listed under chemical substances.

[e] Classified as "inert" gas, i.e., simple asphyxiant.

[f] Not detected in measurements of main process vent gas composition. Detection limit was 1 ppm.

[g] Includes beryllium and mercury.

assuming that the same level of control exists in 1980 as existed in 1974, emissions from the carbon black industry will increase by 14% over that period, i.e.,

$$\frac{\text{Emissions in 1980}}{\text{Emissions in 1974}} = \frac{1.76 \times 10^6}{1.54 \times 10^6} = 1.14$$

SECTION III

SOURCE DESCRIPTION

A. PRODUCT DESCRIPTION

Carbon blacks are essentially elemental carbon in the form of nearly spherical particles of colloidal dimensions. All carbon blacks possess similar properties, and the distinction between the various grades is one of degree rather than kind. In determining the utility of carbon blacks for commercial applications, the most important properties are: (1) particle size; (2) surface area; (3) extent of particle-to-particle association (structure); and (4) surface condition. The basic physical and chemical properties of carbon blacks are described below.

1. Physical Properties

a. Particle Size - The most important physical property of carbon black from the standpoint of commercial applications is particle size. The average particle size of unagglomerated oil furnace blacks ranges from 18 nm to 55 nm, as can be seen in Table 2.[2] For comparison, the properties of carbon blacks produced by the gas furnace, thermal, and

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[2] Smith, W. R., and D. C. Bean. Carbon Black. In: Kirk-Othmer Encyclopedia of Chemical Technology, Second Edition, Vol. 4. John Wiley & Sons, Inc., New York, New York, 1964. pp. 243-282.

Table 2. TYPICAL PROPERTIES OF CARBON BLACKS[2]

Grade	Symbol[a]	Mean particle diameter, nm	Surface area N_2 adsorption, m^2/g	Oil absorption, cm^3/g	Nigrometer reading (unitless)	Volatile matter, %	pH	Benzene extract, %
Oil furnace blacks								
Super abrasion furnace	SAF	18 to 21	90 to 125	1.5	86	1.0	8 to 9	0.05
Intermediate super abrasion furnace	ISAF	22 to 25	115	1.3	88	1.0	8 to 9	0.05
Intermediate super abrasion furnace - low structure	ISAF-LS	20 to 23	110 to 130	0.8 to 0.9	87	1.5	8 to 9	0.05 to 0.10
Intermediate super abrasion furnace - high structure	ISAF-HS	22.5	110 to 120	1.4 to 1.6	88	1.5	8 to 9	0.05
High abrasion furnace	HAF	26 to 30	74 to 100	1.15	90	1.5	8 to 9	0.05
High abrasion furnace - low structure	HAF-LS	25 to 26.5	85 to 110	0.7 to 0.8	87	1.5	8 to 9	0.05
High abrasion furnace - high structure	HAF-HS	22 to 25	80	1.4 to 1.6	90	1.5	8 to 9	0.05
Fast extruding furnace	FEF	40 to 45	40 to 45	1.3 to 1.4	95	1.0	9	0.05
General purpose furnace	GPF	50 to 55	25 to 30	0.9	97	1.0	9	0.05
Conductive furnace	CF	21 to 29	125 to 200	1.3	86 to 93	1.5 to 2	8 to 9	0.06
Gas furnace blacks[b]								
Fine furnace	FF	40 to 50	40 to 50	0.9 to 1.1	90	1.0	5 to 9	0.05
High modulus furnace	HMF	60	30 to 40	0.85	95	1.0	8 to 9	0.10
Semireinforcing furnace	SRF	60 to 80	25 to 30	0.7 to 0.8	97	1.0	8 to 9	0.15
Thermal blacks								
Fine thermal	FT	180	13	0.3 to 0.5	107	0.5	9	1.75
Medium thermal	MT	470	7	0.3 to 0.5	110	0.5	8	0.3
Channel blacks[c]								
High color channel	HCC	9 to 14	400 to 1,000	2 to 4	58 to 69	5 to 16	3 to 4	None
Medium color channel	MCC	15 to 17	320 to 550	1.5	70 to 78	5 to 10	4 to 5	None
Regular color channel	RCC	22 to 29	100 to 140	1.1	80 to 85	5	5	None
Easy processing channel	EPC	29 to 30	100	1.0	85	5	5	None
Medium processing channel	MPC	25 to 28	110 to 120	1.0	83	5	5	None
Medium flow channel	MFC	23 to 25	200 to 210	1.1	80 to 83	7 to 8	4	None
Long flow channel	LFC	22 to 28	300 to 360	1.2	80 to 84	12	3.5	None

[a] ASTM numbers corresponding to the industry classification symbols are shown in Appendix D.

[b] Gas furnace blacks are no longer available. Similar blacks are now made by the oil furnace process (personal communication, H. J. Collyer, Cabot Corporation, Billerica, Massachusetts, 11 May 1977).

[c] Channel blacks are no longer produced domestically; however, they are still available on the international market (personal communication, H. J. Collyer, Cabot Corporation, Billerica, Massachusetts, 11 May 1977).

channel processes are also included in the table.[a] The nomenclature used in this table is that of the industry descriptive system, which is based on the manufacturing process and performance characteristics of the black. For example, semireinforcing furnace black (SRF) denotes a black with intermediate reinforcing properties in rubber that is produced by the furnace process. The American Society for Testing and Materials (ASTM) has also established a comprehensive nomenclature system for carbon blacks which is given in Appendix D.

Particle size is usually measured with an electron microscope, and the arithmetic mean diameter is reported. The particle sizes tend to be log-normally distributed, and the geometric standard deviation increases with mean particle size.[3,4] Typical particle size distributions are shown in Figure 2.

Particle size is of primary importance in determining the reinforcement properties of carbon blacks in rubber compounds. Small particle size blacks impart high tensile strength and abrasion resistance to rubber, but they are difficult to mix and process. The fully reinforcing blacks (SAF, ISAF, HAF), which provide maximum abrasion resistance (for example, in tire tread), range in particle size from about 18 nm to 30 nm.

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[a] Gas furnace blacks and, to a large extent, channel blacks have been replaced by similar blacks made by the oil furnace process. However, channel blacks are still used in some applications. For example, federal regulations specify the use of channel blacks in certain food processing operations.

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[3] Davidson, H. W., P. K. C. Wiggs, A. N. Churchouse, F. A. P. Maggs, and R. S. Bradley. Manufactured Carbon. Pergamon Press, New York, New York, 1968. pp. 1-55.

[4] Matsubayashi, E. Carbon Black. Sekiyu Gakkai Shi, 16(5):381-386, 1973.

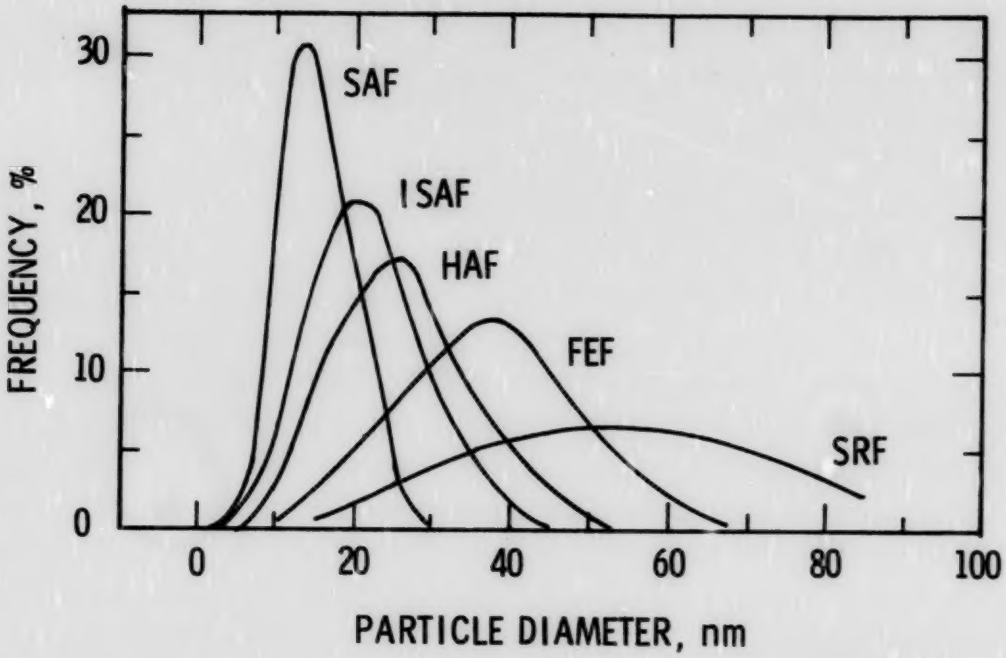

Figure 2. Carbon black particle size distributions for various industry classifications[4]

b. Surface Area - The external surface area of carbon black particles can be calculated from the particle diameter. The total area (internal plus external) is usually measured by gas-adsorption techniques, such as that of Brunauer, Emmett, and Teller (BET). The difference in these two values provides a measure of the internal (porous) surface area.

Low total surface area is desirable in rubber grade blacks since it results in low viscosity and low heat buildup during rubber processing. The high-color and long-flow ink blacks, on the other hand, are highly porous, having total surface areas two to three times greater than their external areas.

Typical specific total surface areas measured by nitrogen adsorption are given in Table 2 for the various grades of black. Some of the newer "improved" carbon blacks have surface areas lower than those of the blacks which they replace and are classified in a different category as to particle size.

c. Structure - The term "structure" refers to the tendency of carbon black particles to form chain- or grape-like aggregates. The forces responsible for structure development vary from weak physical attractions to chemical bonds between particles. The degree of structure of a carbon black has a major influence upon the rheology of the carbon black/rubber system formed when the black is added to an elastomer. High structure blacks tend to disperse more readily in elastomers than do blacks having lower structure, which results in faster mixing. It also results in smooth, low die-swell extrusions of the elastomer-carbon black mixture. High structure is of paramount importance in producing rubber compounds with high elastic modulus and high electrical conductivity.

A quantitative measure of structure is obtained from a volume compressibility measurement or from an oil adsorption experiment. These methods measure the void volume in a sample of carbon black which, in turn, is a measure of structure. An example of the oil adsorption method is the soft-ball oil adsorption test. The minimum amount of linseed oil required to make one gram of black cohere into a soft ball when carefully worked with a spatula is measured. Typical values for the various grades of blacks are given in Table 2.

The soft-ball test has now been largely replaced by the dibutyl phthalate (DBP) test (ASTM test number D2414). The DBP test is a fully automated procedure which is carried out with a Cabot Adsorptometer, an electric kneader-mixer equipped with a torque-measuring device.[5] Dibutyl phthalate is added dropwise to a sample of carbon black. At the point of maximum adsorption (the point at which the voids are filled), there is a transition from a free-flowing powder to a semiplastic material which is accompanied by a rapid increase in torque on the mixer. This end point is sensed automatically and the amount of dibutyl phthalate added to the sample is recorded. The resulting values are referred to as DBP numbers.

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[5] Donnet, J. B., and A. Voet. Carbon Black. Marcel Dekker, Inc., New York, New York, 1976. 351 pp.

d. Crystallinity - X-ray diffraction studies have revealed that carbon black is composed of condensed polycyclic aromatic layers. These layers are in the form of crystallites consisting of three to four parallel layers which are oriented randomly about their normal. A carbon black particle with a diameter of 20 nm contains approximately 1,500 crystallites, which are themselves oriented randomly with respect to each other. Thus, it may be said that carbon black particles exhibit two-dimensional crystallinity. They differ in this way from the three-dimensional structure of graphite particles.

Table 3 gives the internal measurements of a typical carbon black particle.[6]

e. Electrical Conductivity - Electrical conductivity is an important property of carbon blacks since they are used in both insulating and antistatic, or conductive, rubber compounds. The resistivity of carbon black at a pressure of 1.034 MPa ranges from a few tenths to 1 ohm-cm, depending principally upon the amount of oxygen complexed on the surface of the black.[2] However, the resistivity of a rubber stock depends primarily upon the number of conducting paths provided by the black particles, and to a lesser extent upon the resistance of the carbon particles in each path. Thus, the resistivity of a rubber compound depends on the loading, particle size, and structure of the carbon black. Channel blacks provide high electrical resistance in rubber while high structure oil furnace blacks provide a high degree of conductivity.

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[6] Mantell, C. L. Carbon and Graphite Handbook. Interscience Publishers, New York, New York, 1968. pp. 76-105.

Table 3. INTERNAL MEASUREMENTS OF A TYPICAL CARBON BLACK PARTICLE[6]

The Carbon Black Particle	
Diameter	20 nm
Molecular weight	5,000,000
Number of crystallites	1,500
The Crystallite	
Diameter	1.7 nm
Thickness	1.2 nm
Distance between planes	0.35 nm
Average number of planes	3.5
Molecular weight	3,000
The Crystallite Plane	
Molecular weight	1,000
Carbon atoms	90
Hexagonal groups	35

f. Density - The bulk density of carbon blacks ranges from 24 to 59 kg/m^3 before pelletizing and from 97 to 171 kg/m^3 after pelletizing.[7] Since carbon black is not a true crystalline solid, its intrinsic density is not precisely defined.

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[7] Drogin, I. Carbon Black. Journal of the Air Pollution Control Association, 18:216-228, 1968.

X-ray diffraction measurements yield a value of 2,180 kg/m^3 for the average density of the crystallites comprising the particle.[2] Helium displacement measurements give values of 1,840 to 2,130 kg/m^3. The value 1,860 kg/m^3 is accepted for most applications, but the value 1,800 kg/m^3 is commonly employed in the rubber industry.

When physical data for carbon black are unavailable, the corresponding values for graphite can be used as an approximation.

g. Jetness - The jetness (darkness) of carbon black, associated with its particle size, increases with decreasing particle size. Quantitative measurements of jetness are made with a nigrometer, which measures the intensity of light reflected by a black-oil dispersion in terms of a standard. The nigrometer reading decreases with increasing jetness. Typical values are given in Table 2.

2. Chemical Properties

Carbon blacks consist of 90% to 99% elemental carbon, with oxygen, hydrogen and sulfur comprising the other major constituents. Analyses of several grades of carbon black are given in Table 4. Residual hydrogen from the hydrocarbon raw material is distributed throughout the particle.[2] It is believed to be bonded to the carbon atoms by true valence bonds, resulting in an unsaturated state.[8] The oxygen is chemisorbed on the surface of the carbon black.[8] Since little oxygen is present in the region of the furnace where the carbon black originates, it follows that the presence of chemisorbed oxygen arises from subsequent adsorption on the surface of the black during processing. The principal oxygen-containing functional groups on the carbon black surface are phenol, quinone, carboxyl, and lactone. Functional group analyses of several blacks are given in Table 5.[8]

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[8] Deviney, M. L. Surface Chemistry of Carbon Black and Its Implications in Rubber Chemistry. A Current Review. Advances in Colloid Interface Science, 2(3):237-259, 1969.

Table 4. COMPOSITION OF TYPICAL CARBON BLACKS[6]

Type	Composition, %			
	Carbon	Oxygen	Hydrogen	Sulfur
Oil furnace blacks				
Super abrasion furnace	97.6	1.01	0.47	0.64
Intermediate super abrasion furnace	97.6	1.17	0.32	0.51
High abrasion furnace	97.9	0.79	0.34	0.59
Fast extruding furnace	98.4	0.58	0.38	0.67
General purpose furnace	98.6	0.21	0.37	0.55
Conductive furnace	97.4	1.18	0.21	0.60
Gas furnace blacks[a]				
Fine furnace	98.2	0.40	0.4	0.01
High modulus furnace	98.8	0.23	0.4	0.23
Semireinforcing furnace	99.2	0.22	0.4	0.00
Thermal blacks				
Fine thermal	99.3	0.10	0.49	0.01
Medium thermal	99.4	0.0	0.36	0.01
Channel blacks[b]				
High color channel	88.0	10.5	0.9	0.57
Low color channel	95.2	3.6	0.6	0.50
Easy processing channel	95.6	3.5	0.6	0.19
Medium flow channel	94.5	4.9	0.5	0.10
Long flow channel	91.6	7.7	0.6	0.12

[a] Gas furnace blacks are no longer available. Similar blacks are now made by the oil furnace process.

[b] Channel blacks are no longer produced domestically; however, they are still available on the international market.

When carbon black is heated progressively from 600°C to 1,500°C, the surface complexes are decomposed and carbon oxides and hydrogen are evolved.[2] The percent weight loss on heating to 927°C is designated the "volatile content." Typical volatile content values are listed in Table 2.

Table 5. FUNCTIONAL GROUP ANALYSES OF CARBON BLACKS[8]

Black type	Functional group content, milliequivalents/g black			
	Phenol	Quinone	Carboxyl	Lactone
ISAF	0.54	0.02	0.02	0.11
HAF-HS	0.11	0.29	0.00	N.A.[a]
LFC	1.30	2.29	0.28	0.24

[a] Not available.

Carbon black may also contain from 0.01% to 0.7% combined and free sulfur, depending on the amount of sulfur-containing compounds present in the raw material.[a] The combined sulfur is apparently inert, but the free sulfur may contribute to crosslinking during the vulcanization of rubber compounds.[2]

Carbon blacks normally have ash contents of a few tenths of a percent. The ash content of channel blacks is approximately 0.01% and consists principally of oxides of iron and silica.[2] The ash content of furnace blacks varies from 0.1% to 1.0%, and arises mainly from the water used for quenching the reaction (see Section III.B). This ash consists of soluble salts of calcium, magnesium, and sodium, and accounts for the basic pH of furnace blacks.[2]

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[a] Two different grades of carbon black, N-351 and N-330, were analyzed for total sulfur in the present study. The N-351 sample contained 1.0% sulfur, while the N-330 sample contained 1.5% sulfur. The high sulfur values are due to the high (3.7%) sulfur content of the oil feedstock.

Furnace blacks also contain an adsorbed component which can be removed by extraction with hot benzene. The following polycyclic organic materials (POM's) have been identified in the benzene extract from a semireinforcing furnace black:[9]

- Anthracene
- Phenanthrene
- Fluoranthene
- Pyrene
- Benzo[mno]fluoranthene
- Chrysene
- Benz[a]anthracene
- 9,10-Dimethylbenz[a]anthracene
- 1,2-Benzopyrene
- 3,4-Benzopyrene
- Perylene
- o-Phenylenepyrene
- 1,12-Benzoperylene
- Anthanthrene
- Coronene

An analysis of a high abrasion furnace black (type N339) revealed a 3,4-benzopyrene content of 23 ppm and a coronene content of 92 ppm.[10] A medium thermal black (type N990) contained 192 ppm 3,4-benzopyrene and 472 ppm coronene.[10] The amounts of benzene extractable material contained in the various grades of carbon black are listed in Table 2.

The POM contents of two oil furnace blacks were measured in the present study as described in Appendix E. The results are given in Table 6.

Other substances found in carbon black in trace amounts are amines, phenols, cyanides, and heavy metals. Analyses of a number of blacks for these substances are presented in Table 7.

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[9] Nau, C. A. Health Studies Relating to Carbon Black. Presented at the Conference on Environmental Aspects of Chemical Use in Rubber Processing Operations, Akron, Ohio, March 12-14, 1975. 13 pp.

[10] Collyer, H. J. Carbon Black and Ecology. Presented at the Conference on Environmental Aspects of Chemical Use in Rubber Processing Operations, Akron, Ohio, March 12-14, 1975. 10 pp.

Table 6. POLYCYCLIC ORGANIC MATTER CONTENTS OF CARBON BLACKS
(composition, ppm by weight)

Compound	ASTM no.	
	N330	N351
Acenaphthylene	–[a]	1.1
Anthracene/phenanthrene	1.3	2.3
Benzo[c]phenanthrene	–[b]	0.7
Benzofluoranthenes	–[a]	–[a]
Benzo[ghi]fluoranthene	–[a]	–[a]
Benzo[ghi]perylene/anthanthrene	–[a]	–[a]
Benzopyrenes and perylene	0.3	5.1
Chrysene/benz[a]anthracene	1.0	9.5
Dibenzanthracenes	–[a]	–[a]
Dibenzo[c,g]carbazole	–[a]	–[a]
Dibenzopyrenes	–[a]	–[a]
Dibenzothiophene	0.2	0.3
Dimethylanthracenes/phenanthrenes	3.8	4.5
7,12-Dimethylbenz[a]anthracene	–[a]	–[b]
Fluoranthene	0.9	6.6
Indeno[1,2,3-cd]pyrene	–[a]	–[a]
Methylanthracenes/phenanthrenes	4.9	1.1
Methylcholanthrene	–[a]	–[a]
Methylfluoranthene/pyrene	0.9	2.8
Pyrene	27	79

[a] Not detected; less than 0.1 ppm.
[b] Not detected; less than 0.2 ppm.

The chemical properties of the carbon black skeleton are similar to those of large polynuclear aromatic molecules. The aromatic basicity of carbon blacks is demonstrated by their ability to reduce weak Lewis acids (e.g., Ag^+, Au^{+3}, and I_2) and the fact that they undergo such aromatic

Table 7. TRACE SUBSTANCE ANALYSES OF CARBON BLACKS
(composition, ppm by weight)

Material	ASTM number							
	N110[a]	N326[a]	N330[a]	N472[a]	N660[a]	N774[a]	N330[b]	N351[b]
Amines	380	280	170	460	260	310		
Phenols	0.00	0.11	0.00	0.04	0.62	0.58		
Cyanides	0.52	0.65	0.14	0.80	0.03	0.05		
Aluminum							225	30
Antimony	<0.5	<1.0	<0.5	<1.0	<0.5	<0.5	0.15	<0.05
Arsenic	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.97	0.34
Barium	<0.1	<0.1	<0.1	<0.5	<0.5	<0.5	285	0.55
Beryllium	<0.01	<0.01	<0.01	<0.05	<0.05	<0.03	<0.05	<0.05
Bismuth	<0.25	<0.25	<0.25	<0.4	<0.25	<0.25	<0.05	<0.05
Boron							8.1	0.07
Bromine							0.10	<0.05
Cadmium	<0.05	<0.05	<0.05	<0.1	<0.05	<0.05	<0.05	<0.05
Calcium							360	26
Cerium							1.2	1.5
Cesium							<0.05	<0.05
Chlorine							4.4	0.30
Chromium	0.75	0.69	0.41	1.04	0.45	0.3	16	4.0
Cobalt	<0.05	<0.05	<0.05	<0.1	<0.05	<0.05	0.30	0.10

Table 7 (continued). TRACE SUBSTANCE ANALYSES OF CARBON BLACKS
(composition, ppm by weight)

Material	ASTM number							
	N110[a]	N326[a]	N330[a]	N472[a]	N660[a]	N774[a]	N330[b]	N351[b]
Copper	<0.15	0.30	0.24	0.02	0.51	0.53	110	13
Dysprosium							<0.05	<0.05
Erbium							<0.10	<0.10
Europium							0.05	<0.05
Fluorine							205	9.0
Gadolinium							<0.05	<0.05
Gallium							0.05	<0.05
Germanium							<0.05	<0.05
Gold							<0.05	<0.05
Hafnium							<0.15	<0.15
Holmium							<0.05	<0.05
Indium								
Iodine							<0.05	<0.05
Iridium							<0.05	<0.05
Iron							400	31
Lanthanum							5.0	4.9
Lead	<0.65	2.5	0.80	0.35	3.3	2.7	2.2	0.45
Lithium							0.70	0.30

Table 7 (continued). TRACE SUBSTANCE ANALYSES OF CARBON BLACKS
(composition, ppm by weight)

Material	ASTM number							
	N110[a]	N326[a]	N330[a]	N472[a]	N660[a]	N774[a]	N330[b]	N351[b]
Lutecium							<0.05	<0.05
Magnesium							16	15
Manganese	<0.50	0.18	0.58	0.47	1.5	1.8	2.0	0.40
Mercury	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.80	0.10
Molybdenum	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	0.20	0.75
Neodymium							1.1	2.7
Nickel	2.5	4.3	11.1	0.49	3.8	4.1	43	2.3
Niobium							<0.05	<0.05
Osmium							<0.05	<0.05
Palladium							<0.05	<0.05
Phosphorus							14	3.5
Platinum							<0.05	<0.05
Potassium							700	12
Praseodymium							1.2	1.1
Rhenium								
Rhodium							<0.05	<0.05
Rubidium							0.85	<0.05
Ruthenium							<0.05	<0.05

Table 7 (continued). TRACE SUBSTANCE ANALYSES OF CARBON BLACKS (composition, ppm by weight)

Material	ASTM number							
	N110[a]	N326[a]	N330[a]	N472[a]	N660[a]	N774[a]	N330[b]	N351[b]
Samarium							<0.05	0.05
Scandium							<0.05	<0.05
Selenium	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.05	<0.05
Silicon							205	95
Silver							13	2.4
Sodium							550	500
Strontium							8.0	0.35
Tantalum							<0.05	<0.05
Tellurium							<0.05	<0.05
Terbium							<0.05	<0.05
Thallium	<0.25	<0.25	<0.25	<0.5	<0.25	<0.25	0.05	<0.05
Thorium							<0.10	<0.10
Thulium							<0.05	<0.05
Tin	<0.02	<0.02	<0.02	<0.15	<0.02	<0.02	46	9.0
Titanium							12	15
Tungsten							<0.10	<0.05
Uranium							<0.05	<0.05
Vanadium	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	1.7	0.25

Table 7 (continued). TRACE SUBSTANCE ANALYSES OF CARBON BLACKS (composition, ppm by weight)

Material	ASTM number							
	N110[a]	N326[a]	N330[a]	N472[a]	N660[a]	N774[a]	N330[b]	N351[b]
Ytterbium							<0.10	<0.05
Yttrium							0.05	<0.05
Zinc	<0.42	0.15	0.50	0.31	4.8	3.9	600	8.5
Zirconium							0.40	<0.05

[a] Data obtained from personal communications with H. J. Collyer, Cabot Corporation, 13 March 1975 and 2 September 1975.

[b] Data obtained in present study. Values for arsenic, mercury, and selenium were obtained by atomic absorption; boron was determined by inductively coupled argon plasma excitation (ICAP); all other values were obtained by spark source mass spectrometry.

NOTE: Blanks indicate value was not determined.

electrophilic substitution reactions as sulfonation and Friedel-Crafts alkylation.[2]

B. PROCESS DESCRIPTION

A flow diagram for the oil furnace carbon black process is presented in Figure 3. The process streams are identified in Table 8, and the process itself is described in the following subsections. A description of the thermal process is given in Appendix B; descriptions of the processes for production of acetylene black and lamp black can be found in Reference 5.

1. Feed Materials

Feed materials used in the oil furnace process consist of petroleum oil (stream 1), natural gas (stream 2), and air (stream 3). In addition, small quantities of alkali metal salts may be added to the oil feed in order to control the degree of structure of the black. In one example, 0.012 g of potassium nitrate per kilogram of carbon black was used. (Personal communication with L. B. Evans, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 12 June 1975.) Analyses of typical natural gases used in carbon black manufacture are given in Table 9.[11]

The main petroleum stocks used in carbon black manufacture are:[7] (1) cracked fuel oil from thermal cracking of cycle stocks or the vacuum flash distillate from such cracked fuel oil; (2) thermal or catalytic cycle stocks; and (3) aromatic extracts from catalytic cycle stocks. The ideal raw material

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[11] Miller, S. E., and R. E. Barrett. Sampling and Analysis of Source Emission Samples from a Carbon Black Plant, Final Report. Contract 68-02-1409, Task Order No. 9, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, April 1975. 24 pp. plus appendixes.

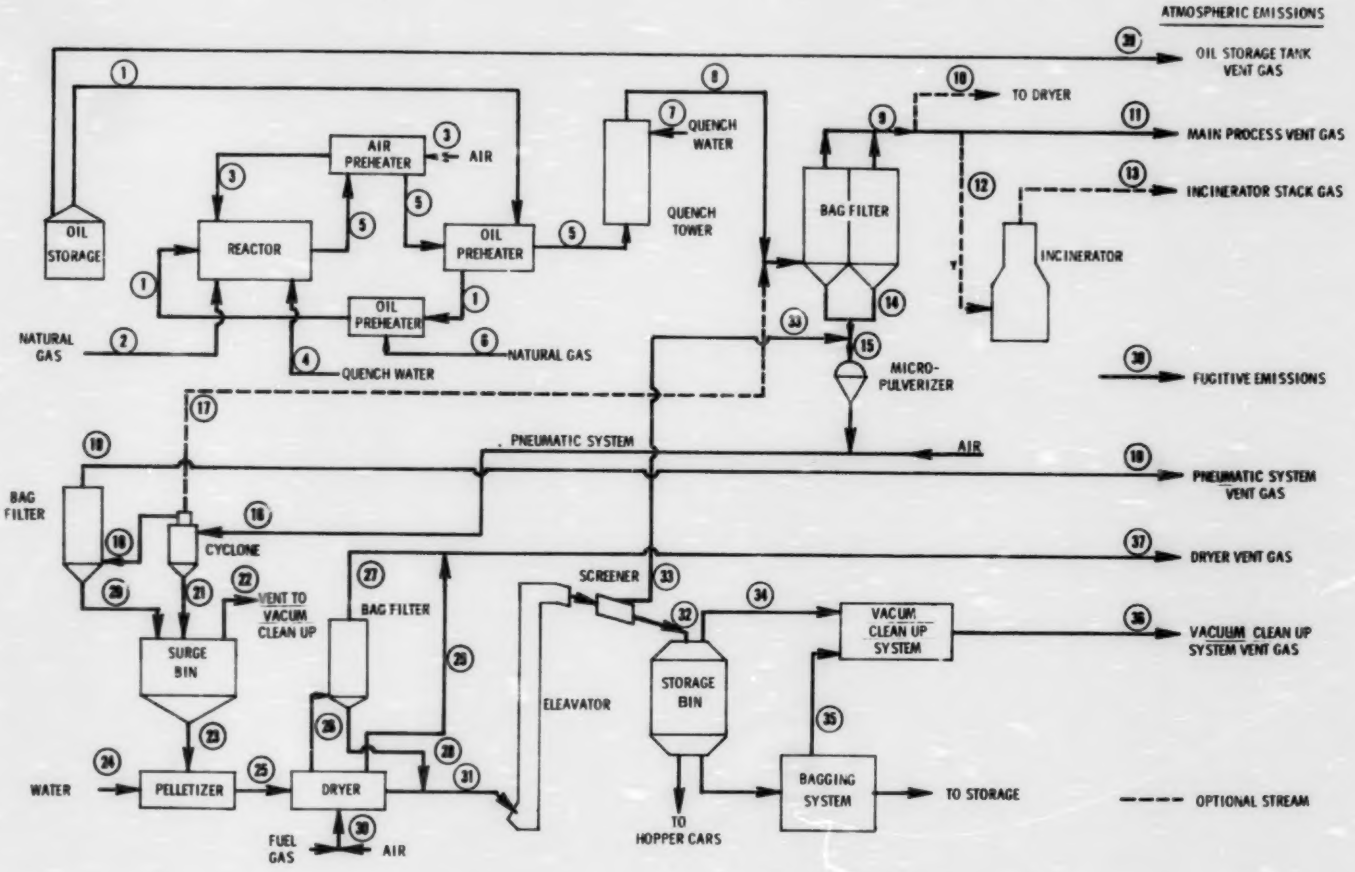
ATMOSPHERIC EMISSIONS
OIL STORAGE TANK VENT GAS
MAIN PROCESS VENT GAS
INCINERATOR STACK GAS
FUGITIVE EMISSIONS
PNEUMATIC SYSTEM VENT GAS
DRYER VENT GAS
VACUUM CLEAN UP SYSTEM VENT GAS
OPTIONAL STREAM
OIL STORAGE
NATURAL GAS
REACTOR
AIR PREHEATER
AIR
OIL PREHEATER
OIL PREHEATER
NATURAL GAS
QUENCH WATER
QUENCH WATER
QUENCH TOWER
BAG FILTER
TO DRYER
INCINERATOR
MICRO-PULVERIZER
AIR
PNEUMATIC SYSTEM
BAG FILTER
CYCLONE
VENT TO VACUM CLEAN UP
SURGE BIN
WATER
PELLETIZER
DRYER
FUEL GAS
AIR
BAG FILTER
ELEAVATOR
SCREENER
STORAGE BIN
TO HOPPER CARS
VACUM CLEAN UP SYSTEM
BAGGING SYSTEM
TO STORAGE
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Figure 3. The oil furnace carbon black process

Table 8. STREAM CODE FOR THE OIL FURNACE PROCESS ILLUSTRATED IN FIGURE 3

Stream	Identification
1	Oil feed
2	Natural gas feed
3	Air to reactor
4	Quench water
5	Reactor effluent
6	Gas to oil preheater
7	Water to quench tower
8	Quench tower effluent
9	Bag filter effluent
10	Vent gas purge for dryer fuel
11	Main process vent gas
12	Vent gas to incinerator
13	Incinerator stack gas
14	Recovered carbon black
15	Carbon black to micropulverizer
16	Pneumatic conveyor system
17	Cyclone vent gas recycle
18	Cyclone vent gas
19	Pneumatic system vent gas
20	Carbon black from bag filter
21	Carbon black from cyclone
22	Surge bin vent
23	Carbon black to pelletizer
24	Water to pelletizer
25	Pelletizer effluent
26	Dryer direct heat source vent
27	Dryer bag filter vent
28	Carbon black from dryer bag filter
29	Dryer indirect heat source vent
30	Hot gases to dryer
31	Dried carbon black
32	Screened carbon black
33	Carbon black recycle
34	Storage bin vent gas
35	Bagging system vent gas
36	Vacuum cleanup system vent gas
37	Dryer vent gas
38	Fugitive emissions
39	Oil storage tank vent gas

Table 9. ANALYSES OF TYPICAL NATURAL GASES USED IN CARBON BLACK MANUFACTURE[7,11]

Component	Composition, mole %	
	1	2
Methane	87.70	91.58
Ethane	3.94	4.96
Propane	2.29	1.68
Iso-butane	0.41	0.23
n-Butane	0.76	0.44
Iso-pentane	0.23	0.10
n-Pentane	0.22	0.11
Hexanes	0.26	0.02
Helium	0.09	N.A.[a]
Carbon dioxide	0.04	0.32
Nitrogen	4.06	0.55
Oxygen	0.00	0.01

[a] Not available.

for the production of modern, high structure blacks is an oil which is highly aromatic, low in sulfur, asphaltenes and high molecular weight resins, and substantially free of suspended ash, carbon, and water. Analyses of several typical liquid hydrocarbon feedstocks are presented in Table 10. A breakdown of the hydrocarbon content of a typical feedstock is presented in Table 11.[12]

In addition to carbon, hydrogen, and sulfur, feedstocks typically contain from 0.002% to 0.1% ash.[13] An analysis of

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[12] Whitsel, T. S. Theoretical Aspects of Carbon Black Manufacture. Rubber Plastics Age. pp. 1209-1212. October 1964.

[13] Gerstle, R. W. Carbon Black Industry, Final Report. Contract 68-02-1321, Task No. 21, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, May 1975. 25 pp.

Table 10. ANALYSES OF TYPICAL LIQUID HYDROCARBON FEEDSTOCKS USED IN CARBON BLACK MANUFACTURE[7,11]

Component	Feedstock				
	1	2	3	4	5
Percent carbon	90.63	90.07	90.37	88.99	90.0
Percent hydrogen	8.27	8.30	7.11	7.48	8.2
Percent sulfur[a]	1.11	1.20	1.77	2.73	2.2
Specific gravity @16°C	1.060	1.054	1.116	1.080	1.087
Molecular weight	270	275	265	240	N.A.[b]
Aromatics, % by weight	72	78.7	85.9	77	N.A.

[a] The increasing scarcity of low sulfur fuels is resulting in the use of higher sulfur-containing feedstocks by the carbon black industry. A sample of a liquid feedstock was analyzed and found to contain 3.7% sulfur.

[b] Not available.

Table 11. HYDROCARBON CONTENT OF A TYPICAL CARBON BLACK FEEDSTOCK OIL[12]

Component	Composition, weight %
Paraffins	1.4
Monocyclics	
Saturated	12.6
Aromatic	6.3
Dicyclics	
Saturated	6.6
Aromatic	6.1
Tricyclics	
Saturated	4.5
Aromatic	18.8
Polycyclics	
Aromatic	43.7
TOTAL	100.0

the ash content in a typical carbon black feedstock oil was made in the present study and is presented in Table 12. All concentrations were obtained by spark source mass spectrometry (SSMS), with the exception of those for arsenic, mercury, and selenium, which were obtained by atomic absorption (AA), and boron, which was obtained by inductively coupled argon plasma excitation (ICAP).

Vapor pressure data for a typical liquid feedstock are given in Table 13.

Typical oil, air, and natural gas feed ratios used in the oil furnace process are listed in Table 14 for the various grades of black.

In addition to the feed materials, quench water (stream 4) is sprayed into the reactor near its outlet to cool the reaction products. A sample of quench water obtained in the present study was analyzed for trace elements in the same manner as described above for the carbon black feedstock oil. The results of the analysis are given in Table 15.

2. Reactor

The reactor for the oil furnace process consists of a refractory-lined steel furnace which is from 1.5 m to 9 m in length and 0.15 m to 0.76 m in internal diameter.[2,7] To provide maximum efficiency, the furnace and burner are designed to separate, insofar as possible, the heat generating reaction from the carbon forming reaction. Thus, the natural gas feed (stream 2 in Figure 3) is burned to completion with preheated air (stream 3) to produce a temperature of 1320°C to 1540°C.[11] The reactor is designed so that this zone of complete combustion attains a swirling motion, and the oil feed (stream 1), preheated to 200°C to 370°C,[2,7] is

Table 12. TRACE ELEMENT CONTENT OF A CARBON BLACK FEEDSTOCK

Element	Concentration in feedstock oil, ppm by weight
Aluminum	12
Antimony	<0.05
Arsenic	0.50
Barium	0.25
Beryllium	<0.05
Bismuth	<0.05
Boron	0.10
Bromine	<0.05
Cadmium	<0.05
Calcium	5.0
Cerium	0.70
Cesium	<0.05
Chlorine	0.30
Chromium	1.8
Cobalt	<0.05
Copper	1.6
Dysprosium	<0.05
Erbium	<0.05
Europium	<0.05
Fluorine	4.6
Gadolinium	<0.3
Gallium	<0.05
Germanium	<0.05
Gold	<0.05
Hafnium	<0.10
Holmium	<0.05
Indium	not determined
Iodine	<0.05
Iridium	<0.05
Iron	5.5
Lanthanum	2.5
Lead	0.30
Lithium	<0.05
Lutecium	<0.05
Magnesium	11
Manganese	<0.05
Mercury	0.16
Molybdenum	0.10
Neodymium	0.40
Nickel	5.5
Niobium	<0.05
Osmium	<0.05

Table 12 (continued). TRACE ELEMENT CONTENT OF A CARBON BLACK FEEDSTOCK

Element	Concentration in feedstock oil, ppm by weight
Palladium	<0.05
Phosphorus	4.3
Platinum	<0.05
Potassium	8.0
Praseodymium	0.15
Rhenium	not determined
Rhodium	<0.05
Rubidium	<0.05
Ruthenium	<0.05
Samarium	<0.05
Scandium	<0.05
Selenium	<0.05
Silicon	360
Silver	0.15
Sodium	20
Strontium	0.10
Tantalum	<0.05
Tellurium	<0.05
Terbium	<0.05
Thallium	<0.05
Thorium	<0.05
Thulium	<0.05
Tin	29
Titanium	4.2
Tungsten	<0.05
Uranium	<0.05
Vanadium	0.10
Ytterbium	<0.05
Yttrium	<0.05
Zinc	5.5
Zirconium	0.05

Table 13. VAPOR PRESSURE DATA FOR TYPICAL LIQUID HYDROCARBON FEEDSTOCK[a]

Temperature, °C	Vapor pressure, kPa
23	0.0
66	1.4
79	2.8
93	3.5
107	6.2
121	8.3
135	10.3

[a] Personal communication with L. B. Evans, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 12 June 1975.

Table 14. TYPICAL FEED RATIOS IN THE OIL FURNACE PROCESS[7]

Grade of black	Air/gas/oil volumetric ratios
SAF	7,466/482/1
ISAF	6,481/416/1
HAF	5,734/358/1
FEF	2,990/ 20/1

sprayed into the center of the zone. Preheating is accomplished by heat exchange with the reactor effluent and/or by means of a gas-fired heater. The oil is cracked to carbon and hydrogen with side reactions producing carbon oxides, water, methane, acetylene and other hydrocarbon products. The heat transfer from the hot combustion gases to the atomized oil is enhanced by highly turbulent flow in the reactor.

Table 15. TRACE ELEMENT CONTENT OF A CARBON BLACK QUENCH WATER

Element	Concentration in quench water, ppm by weight
Aluminum	0.005
Antimony	<0.001
Arsenic	0.008
Barium	0.026
Beryllium	<0.001
Bismuth	<0.001
Boron	0.10
Bromine	0.10
Cadmium	0.007
Calcium	2.8
Cerium	<0.001
Cesium	<0.001
Chlorine	33
Chromium	<0.001
Cobalt	<0.001
Copper	0.017
Dysprosium	<0.001
Erbium	<0.001
Europium	<0.001
Fluorine	0.4
Gadolinium	<0.001
Gallium	<0.001
Germanium	<0.001
Gold	<0.001
Hafnium	<0.001
Holmium	<0.001
Indium	not determined
Iodine	0.003
Iridium	<0.001
Iron	0.56
Lanthanum	<0.001
Lead	0.001
Lithium	not determined
Lutecium	<0.001
Magnesium	1.07
Manganese	0.11
Mercury	<0.001
Molybdenum	0.003
Neodymium	<0.001
Nickel	<0.001
Niobium	<0.001

Table 15 (continued). TRACE ELEMENT CONTENT OF CARBON BLACK QUENCH WATER

Element	Concentration in quench water, ppm by weight
Osmium	<0.001
Palladium	<0.001
Phosphorus	3.0
Platinum	<0.001
Potassium	1.6
Praseodymium	<0.001
Rhenium	not determined
Rhodium	<0.001
Rubidium	<0.001
Ruthenium	<0.001
Samarium	<0.001
Scandium	<0.001
Selenium	<0.001
Silicon	10.5
Silver	<0.001
Sodium	87
Strontium	0.005
Sulfur	32
Tantalum	<0.001
Tellurium	<0.001
Terbium	<0.001
Thallium	<0.001
Thorium	<0.001
Thulium	<0.001
Tin	<0.001
Titanium	0.004
Tungsten	<0.001
Uranium	<0.001
Vanadium	0.001
Ytterbium	<0.001
Yttrium	<0.001
Zinc	0.003
Zirconium	<0.001

The design of the furnace and burner for carrying out this process in an optimum manner constitutes an important part of proprietary carbon black technology. Each manufacturer has developed and patented its own furnace design, a number of which are shown schematically in Figures 4[14-18] and 5.[19]

The reactor converts 35% to 65% of the feedstock carbon content to carbon black, depending on the feed composition and the grade of black being produced. The yields are lower for the smaller particle size grades of black. Variables that can be adjusted to produce a given grade of black include operating temperature, fuel concentration, space velocity in the reaction zone, and reactor geometry (which influences the degree of turbulence in the reactor). In addition, the degree of structure of the black can be controlled by the use of modifiers, usually salts of the alkali metals, which are injected into the furnace with the oil feed.[20] A typical set of reactor operating conditions is given in Table 16.[3]

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[14] Krejci, J. C. Carbon Black Process. U.S. Patent 2,632,713 (to Phillips Petroleum Company), March 24, 1953.

[15] Improvements in the Manufacture of Carbon Black. British Patent 669,968 (to Columbian Carbon Company), April 9, 1952.

[16] Braendle, H. A. Manufacture of Carbon Black. U.S. Patent 2,735,753 (to Columbian Carbon Company), February 21, 1956.

[17] Stokes, C. A. Process of Producing Carbon Black and Synthesis Gas. U.S. Patent 2,672,402 (to Cabot Corporation), March 16, 1954.

[18] Williams, I. Process and Apparatus for Making Carbon Black. U.S. Patent 2,625,466 (to J. M. Huber Corporation), January 13, 1953.

[19] Process and Apparatus for the Production of Carbon Black. British Patent 699,406 (to Godfrey L. Cabot Corporation), November 4, 1953.

[20] Friauf, G. F., and B. Thorley. Carbon Black Process. U.S. Patents 3,010,794 and 3,010,795 (to Cabot Corporation), November 28, 1961.

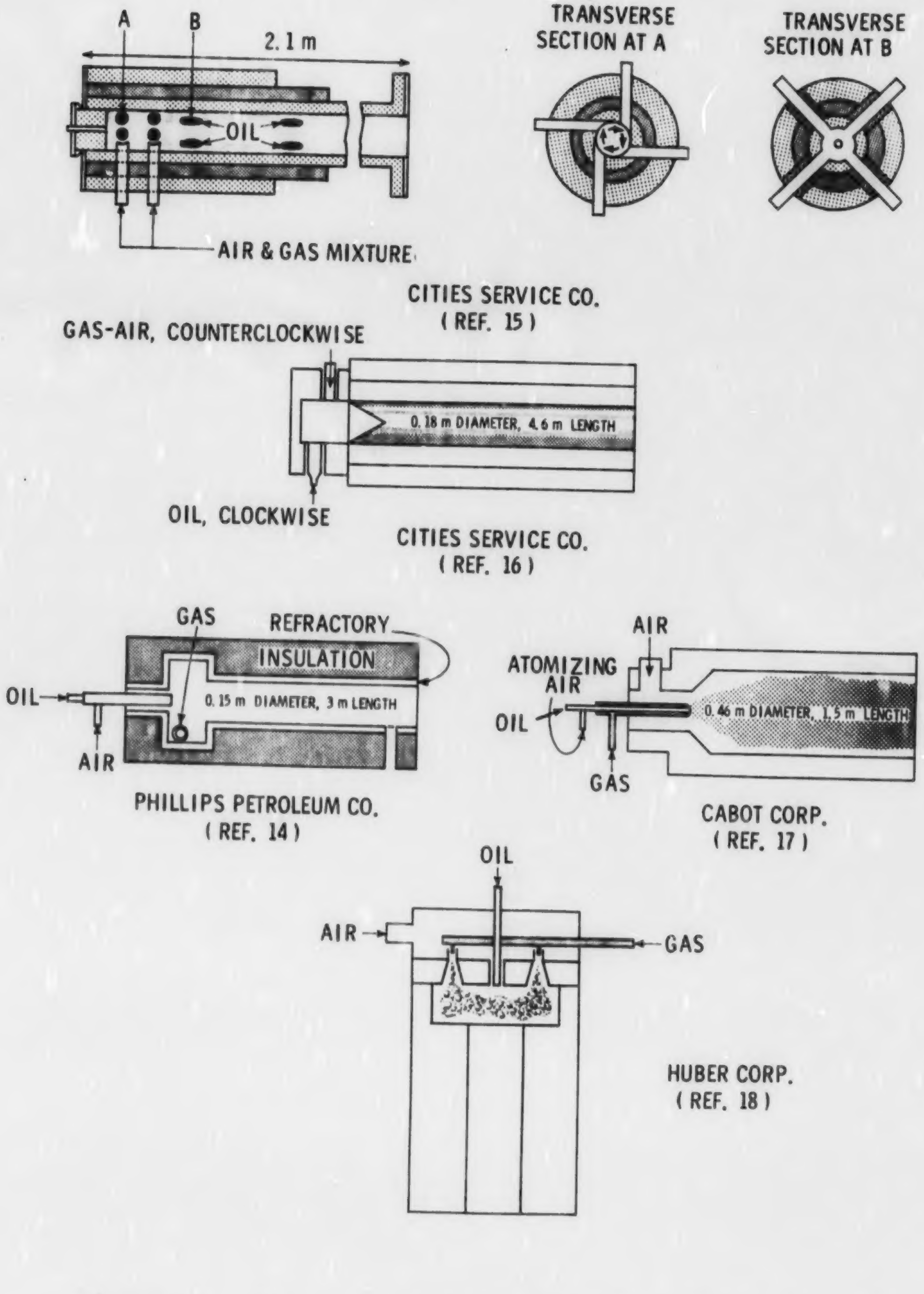
A
B
2.1 m
OIL
AIR & GAS MIXTURE
TRANSVERSE SECTION AT A
TRANSVERSE SECTION AT B
CITIES SERVICE CO.
(REF. 15)
GAS-AIR, COUNTERCLOCKWISE
0.18 m DIAMETER, 4.6 m LENGTH
OIL, CLOCKWISE
CITIES SERVICE CO.
(REF. 16)
GAS
REFRACTORY
INSULATION
OIL
0.15 m DIAMETER, 3 m LENGTH
AIR
PHILLIPS PETROLEUM CO.
(REF. 14)
AIR
ATOMIZING AIR
OIL
0.46 m DIAMETER, 1.5 m LENGTH
GAS
CABOT CORP.
(REF. 17)
OIL
AIR
GAS
HUBER CORP.
(REF. 18)

Figure 4. Five oil furnace process reactor designs

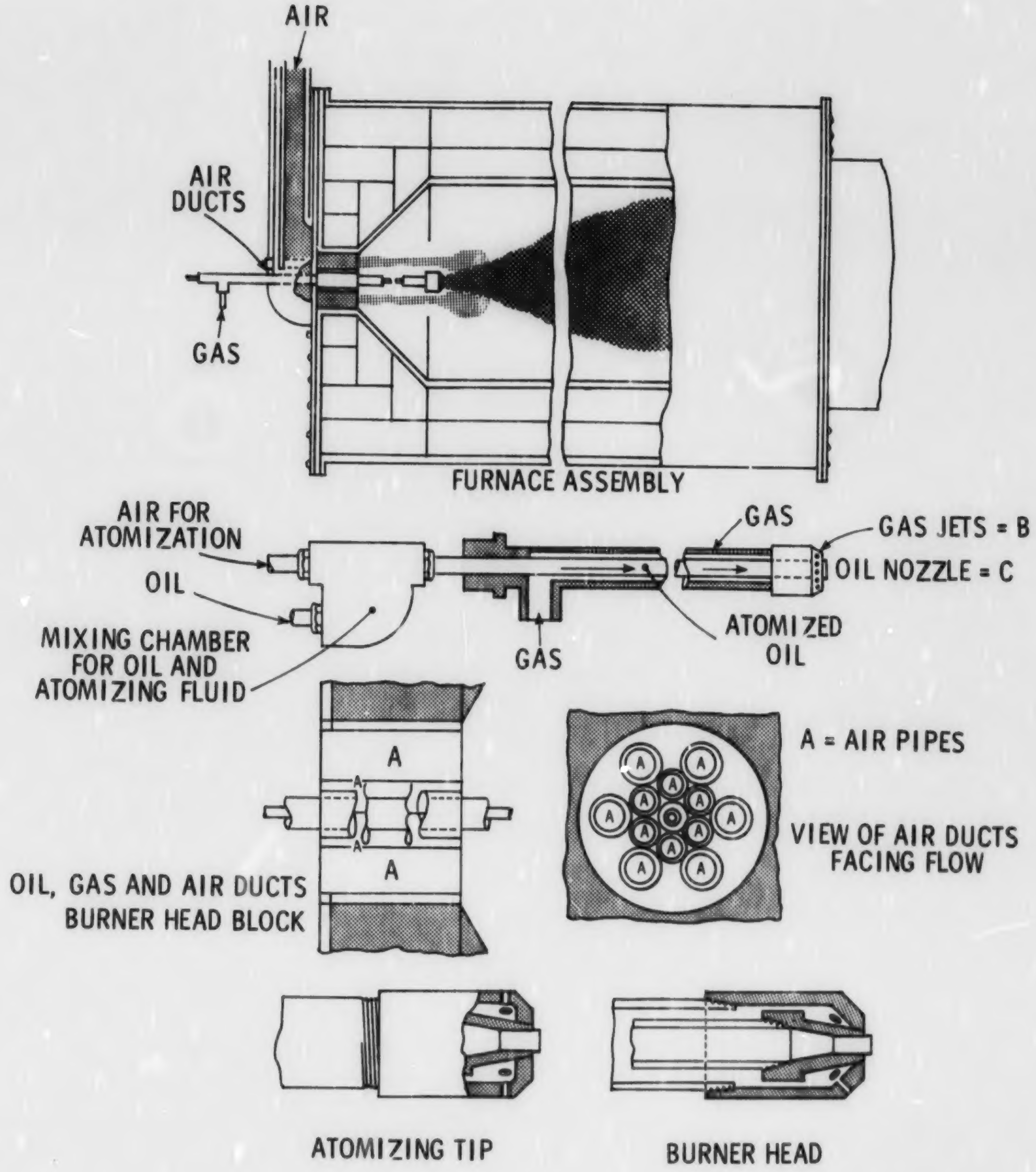
AIR
AIR DUCTS
GAS
FURNACE ASSEMBLY
AIR FOR ATOMIZATION
OIL
MIXING CHAMBER FOR OIL AND ATOMIZING FLUID
GAS
GAS
ATOMIZED OIL
GAS JETS = B
OIL NOZZLE = C
A = AIR PIPES
A
A
VIEW OF AIR DUCTS FACING FLOW
OIL, GAS AND AIR DUCTS BURNER HEAD BLOCK
ATOMIZING TIP
BURNER HEAD

Figure 5. Details of the Cabot reactor[19]

Table 16. TYPICAL REACTOR OPERATING CONDITIONS[3]

Parameter	Value
Type of black produced	HAF
Rate of oil feed	0.76 m^3/hr
Preheat temperature of oil	288°C
Rate of air feed	6,653 m^3/hr
Rate of natural gas feed	623 m^3/hr
Furnace temperature in reaction zone	1,400°C
Rate of carbon black production	390 kg/hr
Yield of black (based on carbon in oil feed)	60%

The hot combustion gases and suspended carbon black are cooled to about 540°C by a direct water spray in the quench area, located near the reactor outlet. The reactor effluent (stream 5 in Figure 3) is further cooled by heat exchange in the air and oil preheaters. It is then sent to a quench tower where direct water sprays finally reduce the stream temperature to 230°C.[7]

3. Product Recovery

Carbon black is recovered from the reactor effluent stream by means of a bag filter unit. Figure 6 is a diagram of a typical unit.[21] The carbon black laden gases from the quench tower (stream 8 in Figure 3) enter the hopper trough below the bag cell plates at 200°C to 230°C. The gases flow into the individual bags of each compartment through the cell

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[21] Schwartz, W. A., F. B. Higgins, Jr., J. A. Lee, R. Newirth, and J. W. Pervier. Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry. Volume 1: Carbon Black Manufacture by the Furnace Process. EPA-450/3-73-006-a, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 1974. 116 pp.

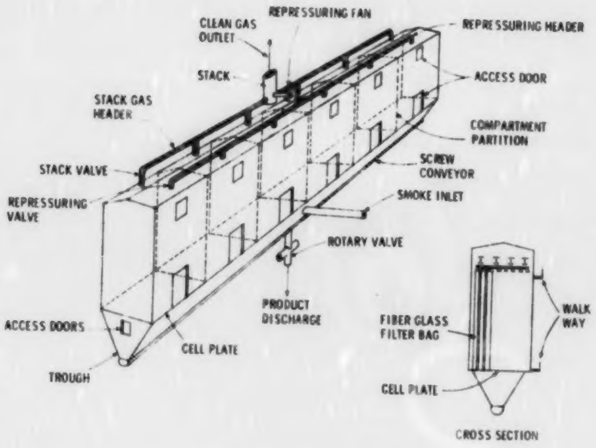
REPRESSURING FAN
CLEAN GAS OUTLET
REPRESSURING HEADER
STACK
ACCESS DOOR
STACK GAS HEADER
COMPARTMENT PARTITION
STACK VALVE
SCREW CONVEYOR
REPRESSURING VALVE
SMOKE INLET
ROTARY VALVE
PRODUCT DISCHARGE
FIBER GLASS FILTER BAG
WALK WAY
ACCESS DOORS
CELL PLATE
TROUGH
CELL PLATE
CROSS SECTION

Figure 6. Bag filter unit for carbon black recovery[21]

plates. The carbon black collects on the inside of the bags and the filtered gas flows through the bags and out the bag filter stacks. During the cleaning cycle of each compartment (see Figure 7), the black is removed from the bag fabric and drops back into the hopper trough. It passes from the hopper through a hammer mill (micropulverizer) that breaks up the lumps and is then transported to the product treatment section of the plant via a pneumatic conveyor system (stream 16).

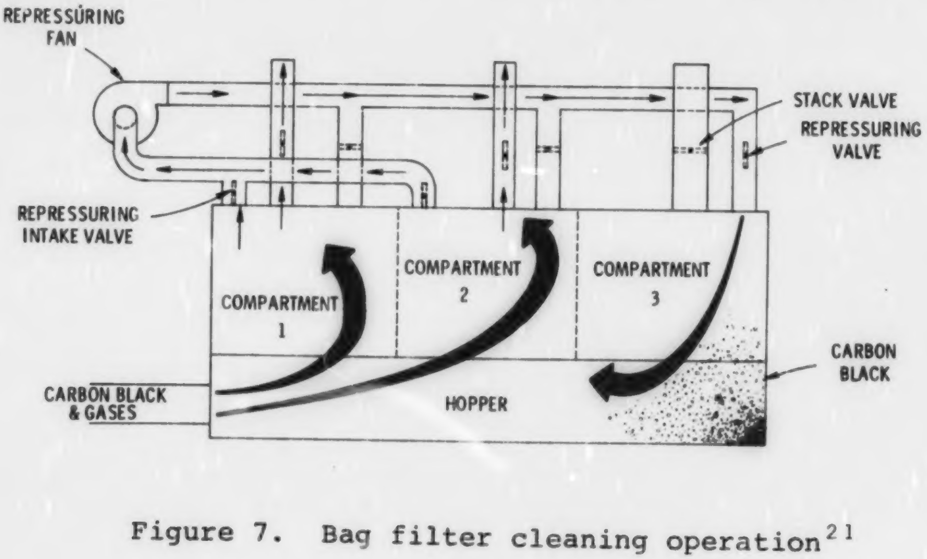
REPRESSURING FAN
STACK VALVE
REPRESSURING VALVE
REPRESSURING INTAKE VALVE
COMPARTMENT 1
COMPARTMENT 2
COMPARTMENT 3
CARBON BLACK
CARBON BLACK & GASES
HOPPER

Figure 7. Bag filter cleaning operation[21]

The bag filter unit consists of from six to 18 compartments, each of which contains 300 to 400 bags. The bags, made of fiber glass coated with a graphite-silicon film, are approximately 14 cm in diameter and 3.2 m long.[21] Each one hangs from the roof of the filter compartment on a metal cap which is tapered on the sides and slightly larger in diameter than the hem around the top of the bag. The bag is wedged around the perimeter of the cap to provide a seal and support for the bag. The bottom of each bag is secured to the cell plate with a snap ring. The entire unit shown in Figure 6 has a single stack. However, some units have a separate stack for each compartment to aid in the location of leaking bags.

The bags are cleaned automatically at 15-minute intervals, with only one compartment on the cleaning cycle at any given time. The cleaning cycle requires 15 to 40 seconds and is accomplished by means of reverse flow and mechanical shaking. Figure 7 shows a three-compartment unit with the third compartment on the cleaning cycle. The gas used for the cleaning operation is taken from the compartments that are on the filtering cycle. The repressuring fan generates sufficient pressure to reverse the gas flow in compartment three.

The exhaust gas from the bag filter unit (stream 9 in Figure 3) is vented directly to the atmosphere in most carbon black plants. Alternatively, it may be sent to a flare or incinerator to reduce the contaminant loading (stream 12). In addition, 13% to 15%[11] of the effluent (stream 10) may be diverted to provide auxiliary fuel for the drying operation, which is discussed below.

4. Product Treatment and Storage

The raw carbon black collected in the bag filter unit must be further processed to become a marketable product. After passing through the pulverizer, the black has a bulk density of 24 to 59 kg/m^3, depending on the grade being produced,[7] and it is too fluffy and dusty to be transported. It is therefore converted into pellets or beads with a bulk density of 97 to 171 kg/m^3.[7] In this form it is dust-free and sufficiently compacted for shipment.

The carbon black is collected from the pneumatic system (stream 16) by means of a cyclone, a bag filter, or a cyclone and bag filter in combination. When a cyclone is used, the exhaust gas (stream 17) is recycled to the primary bag filter unit. When a bag filter is used, the exhaust gas (stream 19) is vented to the atmosphere. The recovered carbon black is collected in a covered surge bin. (In some plants the micro-pulverizer is located between the pneumatic system recovery device[s] and the surge bin.) The cyclone separator typically has a diameter of 1.4 m and a height of 3 m to 4 m.[7] The bag filter is designed to operate at 1.2 m^3/min per square meter of fabric area.[7] Since the gas stream is at approximately ambient temperature, fiber glass bags are not required on this unit, and wool, cotton, or Orlon® bags are used.

The carbon black is fed from the surge bin via a screw conveyor to the pelletizer, where it is mixed with one part of water to two parts of black. A binding agent such as molasses, sugar, dextrin, or starch, may be added to the pelletizing water.[22,23] Typical amounts are 0.001 kg to 0.004 kg per kg

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[22] Day, J. V. Carbon Black Pellets and a Process for Their Manufacture. U.S. Patent 2,850,403 (to Cabot Corporation), September 2, 1958.

[23] Alleman, C. E. Carbon Black Pelletizing by Controlling Power to the Pelletizer Motor. U.S. Patent 3,266,873 (to Phillips Petroleum), August 16, 1966.

of carbon black. The pelletizer is a horizontal housing that contains a revolving axial shaft with pins or spikes mounted on its periphery. Agitation by the pins causes the mixture of carbon black and water to form nearly spherical particles 1.6 mm to 3.2 mm in diameter.[7] The pellets are then conveyed to a dryer for removal of the water. The moisture content of the dried pellets (stream 31) is 1% or less by weight (personal communication, H. J. Collyer, Cabot Corporation, Billerica, Massachusetts, 11 May 1977).

Typical dryers are of the rotating horizontal drum type and operate at 190°C to 230°C depending on the product load.[7] The dryers are fueled by natural gas, which may be augmented by a portion of the main process vent gas. From 35% to 70% of the combustion gas is charged directly to the interior of the dryer.[21] After passing through the dryer, this stream (stream 26) is sent to a bag filter for removal of entrained carbon black before being vented to the atmosphere. The remaining 30% to 65% of the combustion gas (stream 29) acts as an indirect heat source for the dryer and is vented directly to the atmosphere.

The dried, pelletized carbon black (stream 31) is screened and sent to a covered storage bin via a bucket elevator. Oversize pellets are removed in the screener and recycled (stream 33) to the pulverizer. From the product storage bin, the carbon black can be loaded into railroad hopper cars for bulk shipment or sent to a vacuum bagging system which is hermetically sealed to prevent emission of black. The black is packaged in 22.7-kg paper sacks made of 3-ply kraft paper.

The bags are then sent to storage to await shipment. Some black is also shipped in collapsible rubber containers (Sealdbins®) and in metal Tote® bins.

5. Vacuum Cleanup System

Most (two-thirds[21]) carbon black plants employ a plantwide vacuum cleanup system to minimize emissions of carbon black resulting from spills and leaks. The storage bins and bagging operation can also be vented to this system. A typical system is shown schematically in Figure 8. Multiple hose connections on a vacuum line throughout the plant allow most carbon black spills to be recovered. The recovered black is passed through a grit separator where dirt and other foreign matter is removed. The black is then separated from the air stream by means of a cyclone and/or filter. After passing through a grinder, the black is recycled to the micro-pulverizer in the main process sequence. The filtered air stream from the vacuum system is vented to the atmosphere.

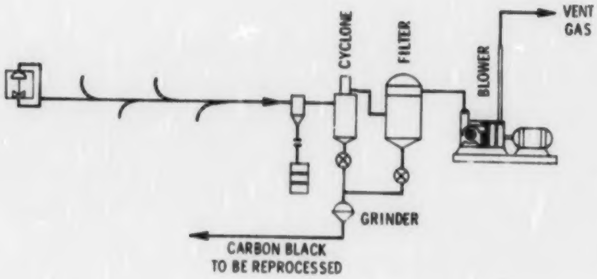

Figure 8. Vacuum cleanup system in modern furnace black plant[21]

6. Storage Tanks

The feedstock and carbon black storage tank requirements for a 4.3 x 10^4 metric tons/yr carbon black plant are summarized in Table 17.

The oil storage tanks are maintained at temperatures ranging from 16°C to 82°C, a typical value being 49°C (personal communication with L. B. Evans, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 12 June 1975). Vapor pressures at these temperatures are typically 0.7 kPa or less, with a maximum value of about 2.8 kPa (see Table 13). The oil storage tanks are vented directly to the atmosphere.

Table 17. TANKAGE REQUIREMENTS FOR A 4.3 x 10^4 METRIC TONS/YR CARBON BLACK PLANT[a]

Tank no.	Material stored	Temperature, °C	Capacity, m^3	Turnovers per year
1	Oil feedstock	49	3,974	6
2	Oil feedstock	49	3,974	6
3	Oil feedstock	49	3,974	6
4	Carbon black	Ambient	1,135	23
5	Carbon black	Ambient	1,135	23
6	Carbon black	Ambient	1,135	23
7	Carbon black	Ambient	1,135	23

[a] Personal communication with L. B. Evans, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 12 June 1975.

Carbon black is stored in covered bins or hoppers at temperatures ranging from ambient to 100°C. Emissions from the vents on these tanks can be controlled by means of the vacuum cleanup system or with bag filters. In some plants these tanks are vented directly to the atmosphere.

7. Plant Shutdown, Turnaround, and Startup

The product recovery bag filters and other emission control equipment in carbon black plants remain in service during startup and shutdown operations, and emissions do not increase during these periods. In some plants the reactors are vented directly to the atmosphere during warmup. Reactor warmup is accomplished by burning natural gas, and the baghouse is put on line before the oil feed is added.[21] Therefore, the only emissions that result from the direct venting are natural gas combustion products.

The repair of process equipment results in the release of carbon black to the atmosphere. These emissions can be minimized by the use of a vacuum cleanup system to clean the equipment immediately after opening for repair.

Carbon black plants typically consist of several parallel equipment trains, each with multiple reactors. Hence, variations in plantwide atmospheric emissions due to individual processing upsets are minimal. The increased particulate emissions resulting from leaks in the product recovery bag filters is an exception.

8. Reactor System Heat Balance

Carbon black production involves two distinct chemical reactions: an exothermic combustion reaction and an endothermic cracking reaction. The net result is an exothermic process which evolves an estimated 24.2 MJ/kg of carbon black produced.[21] Using this value, gross energy balance for the oil furnace reactor system has been estimated, and may be found in Table 18.

C. MATERIALS FLOW

Table 19 presents a material balance for a 4.0×10^4 metric tons/yr oil furnace plant based on data contained in Reference 21 and field sampling data obtained in the present study (see Section IV.B.1). The stream numbers correspond to those given in Figure 3; the optional streams 10, 12, 13, and 17, indicated by dashed lines in Figure 3, are not included. As previously noted, carbon black plants typically consist

Table 18. REACTOR SYSTEM HEAT BALANCE FOR THE OIL FURNACE PROCESS[a]

Heat sources		MJ/kg[b] black
Heat in		
Net heat of reaction		24.2
Oil preheat		1.4
	Total	25.6
Heat out		
Quench to 230°C		17.9
Losses (radiation, preheaters, etc.)		3.5
Incremental heat content[c]		4.2
	Total	25.6

[a] Basis:
1. Material balance presented in Table 19.
2. Reaction zone temperature of 1370°C.

[b] 1 MJ = 1 x 10^6 joules = 948 Btu (see Section X).

[c] Difference in heat content between effluent stream at 230°C and feed streams at 27°C.

of a number of parallel process trains, each containing multiple reactors. The flow rates given in Table 19 are totals of all the process trains.

The sources of atmospheric emissions from the oil furnace process are: the main process vent gas (stream 11), the pneumatic system vent gas (stream 19), the vacuum cleanup system vent gas (stream 36), the dryer vent gas (stream 37), fugitive emissions (stream 38), and the oil storage tank vent gas (steam 39).

D. GEOGRAPHICAL DISTRIBUTION

Carbon black is currently manufactured by eight companies at 30 locations in the United States with a combined capacity

Table 19. MATERIAL BALANCE FOR A 4.0 x 10^4 METRIC TONS/YR CARBON BLACK PLANT

Stream no.:	1	2	3	4	5	6	7
Description:	Oil feed	Gas feed	Air to reactor	Reactor quench	Reactor effluent	Gas to oil preheater	Water to quench tower
Temperature, °C:[a] Gage pressure, kPa:[a]	300[b]	27		16	540[c]	27	16
Component	Flow rates,[d] kg/hr						
Hydrogen					563		
Carbon dioxide					3,518		
Carbon monoxide					7,029		
Hydrogen sulfide					66		
Sulfur oxides					0.6		
Carbon disulfide					66		
Carbonyl sulfide					23		
Methane		2,042			145	–[e]	
Acetylene					174		
Ethane		450				–[e]	
Aromatic oil	8,173						
Nitrogen		211	41,010		41,221		
Oxygen			12,294		739		
Nitrogen oxides					8.2		
Carbon black					5,014		
Water				9,255	14,868		21,597
TOTALS	8,173	2,703	53,304	9,255	73,435	–[e]	21,597

[a] Blanks indicate data not available.

[b] At reactor inlet.

[c] At reactor outlet.

[d] Blanks indicate no mass flow of component.

[e] Data not available.

Table 19 (continued). MATERIAL BALANCE FOR A 4.0 x 10^4 METRIC TONS/YR CARBON BLACK PLANT

Stream no.:	8	9	11	14	15	16	18
Description:	Quench tower effluent	Bag filter effluent	Main process vent gas	Recovered carbon black	Micro-pulverizer feed	Pneumatic system	Cyclone vent gas
Temperature, °C:[a]	230	220	220				
Gage pressure, kPa:[a]	3	0	0				
Component	Flow rates,[d] kg/hr						
Hydrogen	563	563	563				
Carbon dioxide	3,518	3,518	3,518				
Carbon monoxide	7,029	7,029	7,029				
Hydrogen sulfide	66	66	66				
Sulfur oxides	0.6	0.6	0.6				
Carbon disulfide	66	66	66				
Carbonyl sulfide	23	23	23				
Methane	145	145	145				
Acetylene	174	174	174				
Ethane							
Aromatic oil							
Nitrogen	41,221	41,221	41,221			21,560	21,560
Oxygen	739	739	739			6,440	6,440
Nitrogen oxides	8.2	8.2	8.2				
Carbon black	5,014	11	11	5,003	5,503	5,503	550
Water	36,465	36,465	36,465				
TOTALS	95,032	90,029	90,029	5,003	5,503	33,503	28,550

[a] Blanks indicate data not available.

[d] Blanks indicate no mass flow of component.

Table 19 (continued). MATERIAL BALANCE FOR A 4.0 x 10^4 METRIC TONS/YR CARBON BLACK PLANT

Stream no.:	19	20	21	22	23	24	25
Description:	Pneumatic system vent gas	Solids from bag filter	Solids from cyclone	Surge bin vent	Carbon black to pelletizer	Water to pelletizer	Pelletizer effluent
Temperature, °C:[a]						16	
Gage pressure, kPa:[a]							
Component	Flow rates,[d] kg/hr						
Hydrogen							
Carbon dioxide							
Carbon monoxide							
Hydrogen sulfide							
Sulfur oxides							
Carbon disulfide							
Carbonyl sulfide							
Methane							
Acetylene							
Ethane							
Aromatic oil							
Nitrogen	21,560			–[e]			
Oxygen	6,440			–[e]			
Nitrogen oxides							
Carbon black	1.0	549	4,953	–[e]	5,502		5,502
Water						3,000	3,000
TOTALS	28,551	549	4,953		5,502	3,000	8,502

[a] Blanks indicate data not available.

[d] Blanks indicate no mass flow of component.

[e] Data not available.

Table 19 (continued). MATERIAL BALANCE FOR A 4.0 x 10^4 METRIC TONS/YR CARBON BLACK PLANT

Stream no.:	26	27	28	29	30	31	32
Description:	Dryer direct heat source vent	Dryer bag filter vent	Solids from dryer filter	Dryer indirect heat source vent	Hot gases to dryer	Dried carbon black	Screened carbon black
Temperature, °C:[a]	200	190	190	200	220	200	
Gage pressure, kPa:[a]							
Component	Flow rates,[d] kg/hr						
Hydrogen							
Carbon dioxide							
Carbon monoxide	558	558		559	1,117		
Hydrogen sulfide							
Sulfur oxides							
Carbon disulfide							
Carbonyl sulfide							
Methane							
Acetylene							
Ethane							
Aromatic oil							
Nitrogen	8,621	8,621		8,622	17,243		
Oxygen	1,822	1,822		1,822	3,644		
Nitrogen oxides							
Carbon black	455	1.0	454			5,501	5,001
Water	3,435	3,435		435	870		
TOTALS	14,891	14,437	454	11,438	22,874	5,501	5,001

[a] Blanks indicate data not available.

[d] Blanks indicate no mass flow of component.

Table 19 (continued). MATERIAL BALANCE FOR A 4.0 x 10^4 METRIC TONS/YR CARBON BLACK PLANT

Stream no.:	33	34	35	36	37	38	39
Description:	Carbon black recycle	Storage bin vent gas	Bagging systems vent gas	Vacuum cleanup system vent gas	Dryer vent gas	Fugitive emissions	Oil storage tank vent
Temperature, °C:[a]					190		49
Gage pressure, kPa:[a]					0		0
Component	Flow rates,[d] kg/hr						
Hydrogen							
Carbon dioxide							
Carbon monoxide					1,117		
Hydrogen sulfide							
Sulfur oxides							
Carbon disulfide							
Carbonyl sulfide							
Methane							
Acetylene							
Ethane							
Aromatic oil							3.6
Nitrogen		-[e]	-[e]	-[e]	17,243		
Oxygen		-[e]	-[e]	-[e]	3,644		
Nitrogen oxides							
Carbon black	500	-[e]	-[e]	0.2	1.0	0.5	
Water					3,870		
TOTALS	500				25,875	0.5	3.6

[a] Blanks indicate data not available.

[d] Blanks indicate no mass flow of component.

[e] Data not available.

of 1.88 x 10^6 metric tons/yr.[a] Table 20[13,24,25] lists the manufacturers and plant capacities, and the plant locations are shown in Figure 9.[24,25] The population densities of the counties in which the plants are located range from 3 to 539 persons per square kilometer.

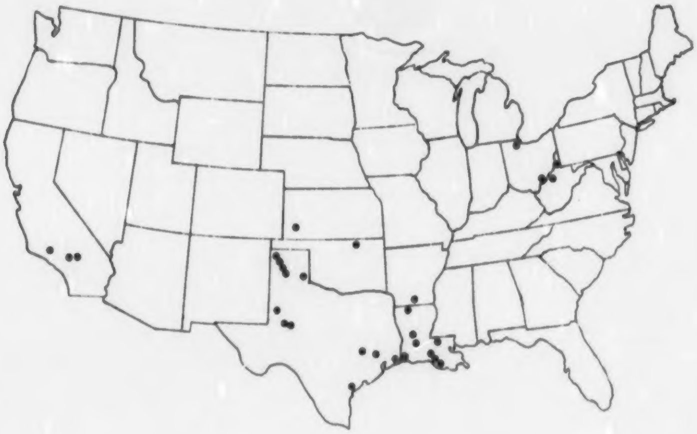

Figure 9. Carbon black plant locations[24,25]

It can be seen that carbon black production is highly localized near sources of hydrocarbon raw materials. Thus, 20 of the 30 plants are located in Texas and Louisiana. These two states accounted for 78% of the total production in 1974.[26] The total production for 1974 is given in Table 21.[26]

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[a] Monsanto's lampblack plant at Camden, New Jersey and Union Carbide's acetylene black plant at Ashtabula, Ohio are not included in these figures. These plants produce small volumes of specialty blacks which are generally not included in carbon black industry statistics by the U.S. International Trade Commission and the Bureau of Mines.

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[24] Chemical Profiles. Carbon Black. Chemical Marketing Reporter, 210(24):9, 1976.

[25] Tire, Rubber, and Carbon Black Plant Locations (Map). Rubber World. 172(2):42-44, 1975.

[26] Carbon Black in 1974. Mineral Industry Surveys, U.S. Department of the Interior, Bureau of Mines, Washington, D.C., 1975.

Table 20. CARBON BLACK PLANTS[13,24,25]

Company	Location	Nominal capacity,[a] 10^3 metric tons/yr	County population density, persons/km^2	Process
Ashland Oil	Arkansas Pass, TX	69.8	25	Furnace
	Belpre, OH	30.4	34	Furnace
	Ivanhoe, LA	108.9	36	Furnace
	Mojave, CA	30.8	15	Furnace
	Shamrock, TX	49.4	3	Furnace
Cabot Corporation	Big Spring, TX	90.7	16	Furnace
	Franklin, LA	174.2	37	Furnace
	Pampa, TX	27.2	11	Furnace
	Ville Platte, LA	88.9	18	Furnace
	Waverly, W.V.	50.8	89	Furnace
Cities Service (Columbian Division)	Conroe, TX	49.9	17	Furnace
	El Dorado, AR	44.4	16	Furnace
	Eola, LA	29.9	17	Furnace
	Franklin, LA	97.1	37	Furnace
	Mojave, CA	22.6	15	Furnace
	Moundsville, W.V.	68.0	47	Furnace
	Seagraves, TX	43.1	3	Furnace
	Ulysses, KS	27.2	4	Furnace
Commercial Solvents	Sterlington, LA	56.7	8	Thermal
Continental Carbon	Bakersfield, CA	32.2	15	Furnace
	Ponca City, OK	55.3	19	Furnace
	Sunray, TX	44.0	6	Furnace
	Westlake, LA	49.4	50	Furnace
J. M. Huber	Bayton, TX	120.6	386	Furnace
	Borger, TX	59.9	10	Furnace
Phillips Petroleum	Borger, TX	144.2	10	Furnace
	Orange, TX	43.1	76	Furnace
	Toledo, OH	36.3	539	Furnace
Sid Richardson Carbon Co.	Addis, LA	36.3	233	Furnace
	Big Spring, TX	54.4	16	Furnace
TOTAL		1,880.7		

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[a] Nominal capacities are approximate since they depend on the type of black being produced.

Table 21. CARBON BLACK PRODUCTION IN 1974[26]

State	Production, 10^3 metric tons	Percent of total
Texas	651	42.3
Louisiana	541	35.2
All others[a]	346	22.5
TOTAL	1,538	100.0

[a] Includes Alabama, Arkansas, California, Kansas, Ohio, Oklahoma, and West Virginia.

SECTION IV

EMISSIONS

A. SELECTED POLLUTANTS

The species considered during this study are listed in Table 22, along with the corresponding threshold limit values obtained from Reference 27. For criteria pollutants, the primary ambient air quality standards are also listed since the latter values are used in the calculation of source severity (see Section IV.C). In addition to emitted species identified in previous studies of the carbon black industry,[11,21] the present study also considered the polycyclic organic materials (POM's) and trace elements listed in Table 22.

B. LOCATION AND DESCRIPTION

1. Main Process Vent Gas

The main process vent gas (stream 11 in Figure 3) is the principal source of atmospheric emissions from carbon black plants. The emissions consist of gaseous reaction products together with residual trace elements from the oil feedstock

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[27] TLVs® Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1976. American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1976. 94 pp.

Table 22. SELECTED POLLUTANTS AND THEIR THRESHOLD LIMIT VALUES

Material emitted	TLV,[27] g/m^3
Criteria pollutants	
Particulate matter	0.01[a] (0.00026[b])
Sulfur oxides	0.013 (0.000365[b])
Nitrogen oxides	0.009 (0.0001[b])
Hydrocarbons	0.00016[b]
Carbon monoxide	0.055 (0.00004[b])
Hazardous pollutants	
Beryllium	0.000002
Mercury	0.00005
Chemical substances	
Hydrogen sulfide	0.015
Carbon disulfide	0.060
Carbonyl sulfide	0.060[c]
Carbon black	0.0035
Methane	-[d]
Acetylene	-[d]
Ethylene	-[d]
Ethane	-[d]
Propylene	-[d]
Propane	-[d]
Butanes	1.4
n-Pentane	1.8
Polycyclic organic matter	
Acenaphthylene	0.0002[e]
Anthracene/phenanthrene	0.0002[e]
Benzo[c]phenanthrene	0.000001[f]

Table 22 (continued). SELECTED POLLUTANTS AND THEIR THRESHOLD LIMIT VALUES

Material emitted	TLV,[27] g/m^3
Polycyclic organic matter (cont'd)	
Benzofluoroanthenes	0.000001[f]
Benzo[ghi]fluoranthene	0.0002[e]
Benzo[ghi]perylene/anthanthrene	0.0002[e]
Benzopyrenes & perylene	0.000001[f]
Chrysene/benz[a]anthracene	0.0002[e]
Dibenzanthracenes	0.000001[f]
Dibenzo[c,g]carbazole	0.000001[f]
Dibenzopyrenes	0.000001[f]
Dibenzothiophene	0.0002[e]
Dimethylanthracenes/phenanthrenes	0.0002[e]
7,12-Dimethybenz[a]anthracene	0.000001[f]
Fluoranthene	0.0002[e]
Indeno[1,2,3-c,d]pyrene	0.000001[f]
Methylanthracenes/phenanthrenes	0.0002[e]
Methylcholanthrene	0.000001[f]
Methylfluoranthene/pyrene	0.0002[e]
Pyrene	0.0002[e]
Trace elements	
Aluminum	-[g]
Antimony	0.0005
Arsenic	0.0005
Barium	0.0005
Bismuth	-[g]
Boron	-[g]
Bromine	0.0007
Cadmium	0.00005
Calcium	-[g]

Table 22 (continued). SELECTED POLLUTANTS AND THEIR THRESHOLD LIMIT VALUES

Material emitted	TLV,[27] g/m^3
Trace elements (cont'd)	
Cerium	-[g]
Cesium	-[g]
Chlorine	0.003
Chromium	0.0005
Cobalt	0.0001
Copper	0.0002
Dysprosium	-[g]
Erbium	-[g]
Europium	-[g]
Fluorine	0.002
Gadolinium	-[g]
Gallium	-[g]
Germanium	-[g]
Gold	-[g]
Hafnium	0.0005
Holmium	-[g]
Iodine	0.001
Iridium	-[g]
Iron	-[g]
Lanthanum	-[g]
Lead	0.00015
Lithium	-[g]
Lutecium	-[g]
Magnesium	-[g]
Manganese	0.005
Molybdenum	0.005
Neodynium	-[g]
Nickel	0.0001
Niobium	-[g]

Table 22 (continued). SELECTED POLLUTANTS AND THEIR THRESHOLD LIMIT VALUES

Material emitted	TLV,[27] g/m^3
Trace elements (con't)	
Osmium	-[g]
Palladium	-[g]
Phosphorus	0.0001
Platinum	0.000002
Potassium	-[g]
Praseodymium	-[g]
Rhodium	0.0001
Rubidium	-[g]
Samarium	-[g]
Scandium	-[g]
Selenium	0.0002
Silicon	0.01
Silver	0.00001
Sodium	-[g]
Strontium	-[g]
Tantalum	-[g]
Terbium	-[g]
Tellurium	0.0001
Thallium	0.0001
Thorium	-[g]
Thulium	-[g]
Tin	0.002
Titanium	-[g]
Tungsten	0.001
Uranium	0.0002
Vanadium	0.0005
Ytterbium	-[g]

Table 22 (continued). SELECTED POLLUTANTS AND THEIR THRESHOLD LIMIT VALUES

Material emitted	TLV,[27] g/m^3
Trace elements (con't)	
Yttrium	0.001
Zinc	-[g]
Zirconium	0.005

[a] Value for "nuisance" particles.

[b] Primary ambient air quality standard.

[c] Assumed equal to value for carbon disulfide.

[d] Classified as "inert" gas, i.e., simple asphyxiant. No TLV established.

[e] Value for coal tar pitch volatiles.

[f] Value for carcinogenic compounds adopted for this program. It corresponds approximately to the minimum detectable limit.

[g] TLV has not been established.

and quench water, and the carbon black fraction which is not recovered in the bag filter units. Emissions data for the main process vent are summarized in Tables 23, 24, and 25.

Table 23 contains the results from a survey of operating plants conducted by the Houdry Division of Air Products and Chemicals,[21] field sampling data obtained by Battelle Columbus Laboratories,[11] and field sampling data obtained by MRC in the present study. In the Battelle study, three sets of measurements were performed on the vent gas from each of the two production trains, one of which was producing N375 grade black while the other was producing N351 grade black. The emission factors given in Table 23 represent the means of these three data sets for each unit, except for the POM value which represents a single measurement. The MRC values represent averages of data obtained in six separate runs; the original data are tabulated in Appendix F. During one run, both N375 and N351 grade blacks were being produced; grade N330 black was being produced during all other runs. The error bounds represent 95% confidence intervals about the mean values.

The emission factors obtained by MRC are based on the assumption that none of the process off-gas is diverted to the dryers. The corresponding emission factors for plants which use the off-gas to fuel the dryers would be approximately 15% lower than those listed in Table 23.

Calculations by plant personnel indicate that the flow rate measurements made in the Battelle study[11] were low by about 35% (personal communication with C. B. Beck, Cabot Corporation, Pampa, Texas, 26 February 1976). If this is indeed the case, the corresponding emission factors in Table 21 are low by approximately 35%. In addition, the emission factors for the unit that was producing N351 grade black represent only 85% of the process off-gas since 15% of the off-gas from that unit was diverted to the dryers.[11]

Emission factors for POM's and trace elements emitted from the main process vent are presented in Tables 24 and 25, respectively. These values were obtained from the field sampling program conducted by MRC as described in Appendix E.

Table 23. EMISSION DATA FOR MAIN PROCESS VENT GAS[11,21]
(emission factor,[a] g/kg)

Material	Plant code number[21]						
	50-1	50-2	50-4	50-5	50-6	50-9	50-10
Hydrogen					162	69	52
Carbon dioxide					1,310	559	419
Carbon monoxide	1,500	1,694	1,713	1,890	2,192	936	701
Hydrogen sulfide	9.5	6.5	10.5	10.5	19	8.0	6.0
Sulfur oxides	3.0	2.0	3.0	3.0	5.0	2.4	1.6
Methane					35	15	11
Acetylene							
Nitrogen							
Argon							
Nitrogen + Argon					12,413	5,295	3,967
Nitrogen oxides							
Carbon black	4.0	4.5	5.0	5.0	3.0	1.3	1.0
Water					8,337	3,557	2,665
Oxygen							
Carbon disulfide							
Carbonyl sulfide							
Ethylene							
Ethane							
Propylene							
Propane							
iso-Butane							
n-Butane							
POM							

[a] Blanks indicate no data reported.

Table 23 (continued). EMISSIONS DATA FOR MAIN PROCESS VENT GAS[11,21]
(emission factor,[a] g/kg)

Material	Plant code number[21]						
	50-11	50-19	50-24	50-25	50-27	50-28	50-29
Hydrogen	101	141	145	183	111	139	59
Carbon dioxide	736	1,238	1,362	1,218	1,077	1,718	857
Carbon monoxide	1,003	1,663	1,710	1,747	1,369	1,864	1,600
Hydrogen sulfide	19	17	16	8.9	Trace	22	20
Sulfur oxides	7.0	0.3	6		Trace	12	7.0
Methane	45	34	45	60	21	36	21
Acetylene	42	129	69	32	6	80	57
Nitrogen			12,308	13,404			
Argon							
Nitrogen + Argon	5,444	10,193			7,163	13,148	11,494
Nitrogen oxides			2.8	1.0		1.2	
Carbon black	3.0	1.2	0.7	0.5		5.1	0.1
Water	4,563				6,872	12,963	
Oxygen			359	638			
Carbon disulfide							
Carbonyl sulfide							
Ethylene							
Ethane							
Propylene							
Propane							
iso-Butane							
n-Butane							
POM							

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[a] Blanks indicate no data reported.

Table 23 (continued). EMISSIONS DATA FOR MAIN PROCESS VENT GAS[11,21] (emission factor,[a] g/kg)

Material	Plant code number[21]	Battelle data[12]		Mean	Range	MRC
	50-30	N375 black	N351 black			
Hydrogen	100	79.6	85.1	110	52 to 183	120 ± 39%
Carbon dioxide	750	504	428	937	419 to 1,718	700 ± 21%
Carbon monoxide	1,625	935	791	1,467	701 to 2,192	1,400 ± 19%
Hydrogen sulfide	10	5.4	6.1	11.5	trace to 22	30 ± 82%
Sulfur oxides	3.0	1.44	0.12	3.6	trace to 12	0.0[b]
Methane	25	20.4	27.4	30	11 to 60	25 ± 47%
Acetylene	32	91.5	93.2	63	6 to 129	45 ± 48%
Nitrogen		5,222	1,577	8,877	4,577 to 13,404	
Argon		85.6	74.1	79.8		
Nitrogen + Argon	9,583	5,308	4,725	8,066	3,967 to 13,148	9,000 ± 19%
Nitrogen oxides				1.7	1.0 to 2.8	0.28 ± 15%
Carbon black	0.1			2.5	0.1 to 5.1	0.11 ± 70%
Water		4,440	4,000	5,924	2,665 to 12,963	6,000 ± 21%
Oxygen		78.7	29.5	276	29.5 to 638	240 ± 99%
Carbon disulfide		10.7	9.67	10.2		30 ± 76%
Carbonyl sulfide		1.46	1.09	1.27		10 ± 99%
Ethylene		1.27	1.29	1.28		1.6 ± 85%
Ethane		<0.03	<0.03	<0.03		0.0[b]
Propylene		0.11	0.11	0.11		0.0[b]
Propane		0.41	0.41	0.41		0.23 + 109% - 100%
Iso-butane		0.20	0.20	0.20		0.10 ± 80%
n-Butane		0.93	0.95	0.94		0.27 ± 57%
n-Pentane						0.0[b]
POM			0.000091	0.000091		0.002 ± 52%
Trace elements						<0.25 ± 43%

[a] Blanks indicate no data reported.

[b] Not detected at detection limit of 1 ppm.

Table 24. EMISSION FACTORS FOR POLYCYCLIC ORGANIC COMPOUNDS IN MAIN PROCESS VENT GAS

Compound	Emission factor, g/kg
Acenaphthylene	$8.0 \times 10^{-4} \pm 142\%$
Anthracene/phenanthrene	$7.0 \times 10^{-5} \pm 170\%$
Benzo[c]phenanthrene	$<2.0 \times 10^{-6} \pm 41\%$
Benzofluoroanthenes	$3.0 \times 10^{-5} \pm 125\%$
Benzo[ghi]fluoranthene	$4.0 \times 10^{-5} \pm 187\%$
Benzo[ghi]perylene/anthanthrene	$2.3 \times 10^{-5} \pm 130\%$
Benzopyrenes & perylene	$3.0 \times 10^{-5} \pm 123\%$
Chrysene/benz[a]anthracene	$9.0 \times 10^{-6} \pm 45\%$
Dibenzanthracenes	$<2.0 \times 10^{-6} \pm 50\%$
Dibenzo[c,g]carbazole	$<2.0 \times 10^{-6} \pm 50\%$
Dibenzopyrenes	$<2.0 \times 10^{-6} \pm 50\%$
Dibenzothiophene	$1.4 \times 10^{-5} \pm 183\%$
Dimethyl-anthracenes/phenanthrenes	$1.4 \times 10^{-4} \pm 128\%$
7,12-Dimethylbenz[a]anthracene	$7.0 \times 10^{-5} \pm 112\%$
Fluoranthene	$6.0 \times 10^{-5} \pm 166\%$
Indeno[1,2,3-cd]pyrene	$<2.0 \times 10^{-6} \pm 50\%$
Methyl-anthracenes/phenanthrenes	$1.0 \times 10^{-4} \pm 100\%$
Methylcholanthrene	$<2.0 \times 10^{-6} \pm 50\%$
Methylfluoranthene/pyrene	$2.3 \times 10^{-5} \pm 86\%$
Pyrene	$5.0 \times 10^{-4} \pm 120\%$
TOTAL	$1.9 \times 10^{-3} \pm 52\%$

Table 25. EMISSION FACTORS FOR TRACE ELEMENTS IN MAIN PROCESS VENT GAS

Element	Emission factor, g/kg
Aluminum	$<2.1 \times 10^{-3}$ ± 20%[a]
Antimony	2.5×10^{-5} ± 78%
Arsenic	4.8×10^{-5} ± 36%
Barium	$<2.2 \times 10^{-3}$ ± 84%[a]
Beryllium	$<4.0 \times 10^{-6}$ ± 8%
Bismuth	$<1.4 \times 10^{-5}$ ± 32%
Boron	$<5.9 \times 10^{-3}$ ± 34%[a]
Bromine	8.8×10^{-6} ± 26%
Cadmium	1.4×10^{-5} ± 40%
Calcium	$<4.0 \times 10^{-2}$ ± 32%[a]
Cerium	5.4×10^{-6} ± 28%
Cesium	$<3.6 \times 10^{-6}$ ± 28%
Chlorine	$<6.0 \times 10^{-3}$ ± 102%[a]
Chromium	$<3.9 \times 10^{-4}$ ± 66%[a]
Cobalt	1.1×10^{-4} ± 57%
Copper	$<1.0 \times 10^{-2}$ ± 113%[a]
Dysprosium	$<2.6 \times 10^{-6}$ ± 33%
Erbium	$<1.0 \times 10^{-5}$ ± 5%
Europium	$<6.5 \times 10^{-6}$ ± 28%
Fluorine	$<2.0 \times 10^{-3}$ ± 52%[a]
Gadolinium	$<2.1 \times 10^{-5}$ ± 47%
Gallium	$<2.2 \times 10^{-6}$ ± 8%
Germanium	$<2.6 \times 10^{-6}$ ± 33%
Gold	$<2.6 \times 10^{-6}$ ± 33%
Hafnium	$<1.6 \times 10^{-5}$ ± 8%
Holmium	$<2.6 \times 10^{-6}$ ± 33%
Indium	–[b]
Iodine	$<3.0 \times 10^{-6}$ ± 128%
Iridium	$<5.8 \times 10^{-6}$ ± 15%
Iron	$<4.5 \times 10^{-3}$ ± 48%[a]

Table 25 (continued). EMISSION FACTORS FOR TRACE ELEMENTS IN MAIN PROCESS VENT GAS

Element	Emission factor, g/kg
Lanthanum	3.9×10^{-6} ± 8%
Lead	$<1.5 \times 10^{-3}$ ± 46%[a]
Lithium	$<1.8 \times 10^{-5}$ ± 76%[a]
Lutecium	$<4.7 \times 10^{-6}$ ± 78%
Magnesium	$<2.07 \times 10^{-2}$ ± 139%[a]
Manganese	$<1.30 \times 10^{-4}$ ± 138%[a]
Mercury	1.50×10^{-4} ± 386%
Molybdenum	$<1.38 \times 10^{-4}$ ± 38%[a]
Neodymium	$<5.8 \times 10^{-6}$ ± 37%
Nickel	1.3×10^{-3} ± 90%
Niobium	$<5.2 \times 10^{-6}$ ± 158%
Osmium	$<7.5 \times 10^{-6}$ ± 55%
Palladium	$<6.0 \times 10^{-6}$ ± 36%
Phosphorus	$<1.00 \times 10^{-2}$ ± 220%[a]
Platinum	$<7.5 \times 10^{-6}$ ± 55%
Potassium	$<3.0 \times 10^{-2}$ ± 137%[a]
Praseodymium	$<4.5 \times 10^{-6}$ ± 119%
Rhodium	$<2.0 \times 10^{-6}$ ± 64%
Rubidium	2.0×10^{-5} ± 191%
Samarium	$<1.4 \times 10^{-5}$ ± 191%
Scandium	$<5.8 \times 10^{-5}$ ± 37%
Selenium	$<1.7 \times 10^{-6}$ ± 66%
Silicon	$<2.0 \times 10^{-2}$ ± 95%[a]
Silver	–[b]
Sodium	$<4.1 \times 10^{-2}$ ± 42%[a]
Strontium	$<3.0 \times 10^{-4}$ ± 262%[a]
Tantalum	$<1.0 \times 10^{-5}$ ± 135%
Terbium	$<2.2 \times 10^{-6}$ ± 19%
Tellurium	$<3.0 \times 10^{-6}$ ± 71%
Thallium	$<6.8 \times 10^{-6}$ ± 59%

Table 25 (continued). EMISSION FACTOR FOR TRACE ELEMENTS IN MAIN PROCESS VENT GAS

Element	Emission factor, g/kg
Thorium	$<1.4 \times 10^{-5}$ ± 81%
Thulium	$<4.4 \times 10^{-6}$ ± 120%
Tin	$<1.3 \times 10^{-3}$ ± 42%[a]
Titanium	2.0×10^{-4} ± 122%
Tungsten	$<2.5 \times 10^{-5}$ ± 45%
Uranium	$<8.0 \times 10^{-6}$ ± 175%
Vanadium	$<1.3 \times 10^{-5}$ ± 138%[a]
Ytterbium	$<9.6 \times 10^{-6}$ ± 32%
Yttrium	$<8.0 \times 10^{-6}$ ± 49%[a]
Zinc	$<5.0 \times 10^{-2}$ ± 135%[a]
Zirconium	$<6.0 \times 10^{-5}$ ± 155%[a]
TOTAL	<0.25 ± 40%

[a] Value reported as upper bound since significant amount of material was found in blank run (see Appendix F).

[b] Not determined.

Each value in these tables represents the mean of three individual runs, and the error bounds represent 95% confidence limits for the mean values. Data for individual sampling runs are tabulated in Appendix F. The values listed in Table 25 are those obtained by spark source mass spectroscopy with the following exceptions: arsenic, mercury, and selenium were determined by atomic absorption (AA) and boron was determined by inductively coupled argon plasma excitation (ICAP).

As noted in Table 25, significant (see Appendix F) amounts of a number of trace elements were found in a blank run which was made as a check on the sampling and analytical procedures. The emission factors for these elements are reported as upper bounds since the actual emission factors must be less than the apparent values, which contain a contribution due to the sampling and/or analytical methods. Those elements listed as upper bounds in Table 25, but which are not footnoted, were present in concentrations below the detection limits of the analytical methods.

The trace element concentrations found in the blank run indicate sample contamination through either the sampling procedure or the analytical work-up procedures. (These procedures are summarized in Appendix E.) One possible source of contamination is the glassware used to collect and process the samples. Silicon, sodium, calcium, magnesium, and aluminum are major constituents of glass. Silicon was also present in the sampling train as silica gel. Thus, the presence of these elements in the blank samples is not surprising. Sources which would account for the anomalous results for other elements, such as phosphorous, potassium, and zinc, have not been identified.

A blank POM run was also made and analyzed. No POM's were detected in the blank samples.

The MRC data are generally consistent with the data from the other two studies in that the MRC measurements fall within the ranges of the values from the Battelle and Houdry studies as shown in Table 23. The only exceptions are NO_x, for which only three values are available for comparison, and hydrogen sulfide. The latter value was verified by means of a sulfur material balance performed by plant personnel using the MRC sampling data. Closure of the material balance was obtained to within less than 5%.

Emissions of sulfur-containing compounds obviously depend on the sulfur content of the feedstock. The increasing scarcity of low-sulfur fuels is forcing the carbon black industry to utilize higher sulfur feedstocks, even though a high sulfur content creates a problem in the maintenance of plant equipment.

The composition of the vent gas also depends upon the type of carbon black produced. As previously noted, the two sets of data obtained by Battelle correspond to two different grades of black, N375 and N351. Differences in the oxygen and sulfur oxides emissions between the two data sets are apparent. However, the information necessary for a more detailed description of the variation in emissions as a function of carbon black type is considered proprietary by the operating company since it would disclose specific details of process design. (Personal communications with H. J. Collyer, Cabot Corporation, Billerica, Massachusetts, 13 March 1975 and 2 September 1975.)

The ranges given for emission factors in Table 23 are indicative of the degree of variability in emissions throughout the carbon black industry. Another measure of variability, the coefficient of variation (standard deviation divided by mean), was also computed from the data in Table 23 for five emitted species, with the following results: hydrogen, 38%; carbon dioxide, 38%; carbon monoxide, 26%; hydrogen sulfide, 53%; methane, 46%.

The composition of a typical vent gas is presented in Table 26, based on the MRC emissions data in Tables 23, 24, and 25.

2. Dryer Vent

The combined dryer vent (stream 37 in Figure 3) is a continuous source of emissions of carbon black that is entrained by the gas stream fed directly to the interior of the dryer. Carbon black emissions are controlled by means of bag filters or scrubbers. Other contaminants in the dryer vent gas result from use of the main process vent gas as a supplementary fuel and from the combustion of impurities in the natural gas fuel for the dryer. These contaminants include sulfur oxides, nitrogen oxides, and the unburned portion of each of the species present in the main process vent gas (see Table 26).

Table 27 summarizes the emissions data obtained from the survey of operating plants given in Reference 21 and from the public files of the Louisiana Air Control Commission. The mean emission factors are 0.17 g/kg for carbon black, 0.23 g/kg for sulfur oxides, and 0.61 g/kg for nitrogen oxides. A mean emission factor for carbon black was also computed considering only those units employing bag filters; it was found to be 0.12 g/kg. The error bounds given for the mean values in Table 27 represent 95% confidence limits for the means.

Table 26. MAIN PROCESS VENT GAS COMPOSITION FOR A TYPICAL CARBON BLACK PLANT

Production rate = 5.1×10^4 metric tons/yr
Temperature = 220°C
Gage pressure = 0 kPa

Component	Concentration, weight %	Emission rate, kg/hr	Emission factor, g/kg
Nitrogen and Argon	51.15	52,700	9,000
Water	34.10	35,100	6,000
Carbon monoxide	7.95	8,200	1,400
Carbon dioxide	3.97	4,100	700
Oxygen	1.35	1,400	240
Hydrogen	0.67	700	120
Acetylene	0.25	260	45
Carbon disulfide	0.17	175	30
Hydrogen sulfide	0.17	175	30
Methane	0.14	145	25
Carbonyl sulfide	0.05	60	10
Ethylene	0.0096	9	1.6
n-Butane	0.0015	1.6	0.27
Nitrogen oxides	0.0015	1.6	0.28
Trace elements	<0.0014	<1.5	<0.25
Propane	0.0012	1.2	0.23
Carbon black	0.0006	0.6	0.11
POM	0.00001	0.012	0.002
Iso-Butane	0.0006	0.6	0.10
Ethane	0.0[a]	0.0[a]	0.0[a]
Propylene	0.0[a]	0.0[a]	0.0[a]
n-Pentane	0.0[a]	0.0[a]	0.0[a]
Sulfur oxides	0.0[a]	0.0[a]	0.0[a]
TOTAL	100.0	103,000	17,670

[a] Not detected at detection limit of 1 ppm.

Table 27. EMISSIONS DATA FOR COMBINED DRYER VENT[21]

Plant code number[21]	Control device	Emission factors, g/kg		
		Carbon black	SO_x	NO_x
50-1	Bag filter	0.06	N.A.[a]	N.A.
50-4	None	0.05	N.A.	N.A.
50-6	Bag filter	0.02	0.04	N.A.
50-7	Bag filter	0.40	0.03	N.A.
50-8	Bag filter	0.03	0.10	N.A.
50-9	Bag filter	0.30	N.A.	N.A.
50-10	None	0.40	0.05	N.A.
50-11	Scrubber	0.01	N.A.	N.A.
50-19	Bag filter	0.01	N.A.	N.A.
50-24	Bag filter	0.10	0.20	N.A.
50-25	Bag filter	N.A.	0.20	N.A.
50-26	Bag filter	0.02	0.50	N.A.
50-27	Bag filter	N.A.	N.A.	Trace
50-28	Scrubber	0.70	0.20	1.10
-[b]	Bag filter	0.10	0.54	0.12
-[b]	Bag filter	N.A.	0.45	0.61
Mean		0.17 ± 77%	0.23 ± 60%	0.61 + 200% - 100%
Range		0.01 to 0.70	0.03 to 0.54	trace to 1.10
Mean for units with bag filters		0.12 ± 89%		

[a] Not available.

[b] Data obtained from public files of Louisiana Air Control Commission.

3. Pneumatic System Vent

The pneumatic system vent gas (stream 19 in Figure 3) is a continuous source of carbon black emissions. The pneumatic system conveys the carbon black from the product recovery bag filters to the product treatment area of the plant. The transported carbon black is removed from the entraining air by means of a cyclone and/or a bag filter. In the latter case the filtered air stream is vented to the atmosphere. Residual carbon black is the only contaminant present in this stream.

Table 28 summarizes the emissions data contained in the survey of carbon black plants reported in Reference 21. The mean carbon black emission factor for the six plants supplying data is 0.29 g/kg. The values range from 0.06 g/kg to 0.70 g/kg. The 95% confidence limits about the mean are ±93%.

Table 28. EMISSIONS DATA FOR PNEUMATIC SYSTEM VENT[21]

Plant code number	Control device	Carbon black emission factor, g/kg
50-6	Bag filter	0.70
50-7	Bag filter	0.24
50-9	Bag filter	0.17
50-10	Bag filter	0.50
50-29	Bag filter	0.06
50-30	Bag filter	0.07
Mean		0.29 ± 93%
Range		0.06 to 0.70

4. Oil Storage Tank Vents

Estimates of hydrocarbon emissions from the oil feedstock storage tank vents (stream 39 in Figure 3) for a 4.3 x 10^4 metric tons/yr carbon black plant are presented in Table 29. These estimates were obtained using the data in Tables 13 and 17 together with the empirical correlations for petrochemical

Table 29. OIL STORAGE TANK WORKING AND BREATHING LOSSES FROM A 4.3 x 10^4 METRIC TONS/YR CARBON BLACK PLANT

Vapor pressure, kPa	Emission rate, kg/hr	Emission factor, g/kg
0.7	3.6	0.72
1.4	6.0	1.21
2.8	10.1	2.06

losses from storage tanks which have been developed by the American Petroleum Institute.[28-32] Values were calculated for three different oil vapor pressures in order to cover the range of values expected for different feedstocks and storage temperatures. The estimated accuracy of the empirical correlations is ±10%.[28-32]

The oil storage tanks are vented directly to the atmosphere in all carbon black plants. Control could be achieved by means of conservation vents or floating roof tanks. However, all carbon black feedstock storage tanks meet EPA New Source Performance Standards for these emissions points (personal communication, C. B. Beck, Cabot Corporation, Pampa, Texas, 26 February 1976).

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[28] Evaporation Loss from Fixed Roof Tanks. Bulletin 2518, American Petroleum Institute, New York, New York, 1962. 38 pp.

[29] Use of Variable Vapor Space Systems to Reduce Evaporation Loss. Bulletin 2520, American Petroleum Institute, New York, New York, 1964. 14 pp.

[30] Petrochemical Evaporation Loss from Storage Tanks. Bulletin 2523, American Petroleum Institute, New York, New York, 1969. 14 pp.

[31] Evaporation Loss from Floating Roof Tanks. Bulletin 2517, American Petroleum Institute, New York, New York, 1962. 13 pp.

[32] Evaporation Loss in the Petroleum Industry - Causes and Control. Bulletin 2513, American Petroleum Institute, New York, New York, 1959. 57 pp.

5. Vacuum Cleanup System Vent

The vacuum cleanup system vent (stream 36 in Figure 3) is a semicontinuous source of carbon black emissions. This system is used to pick up loose carbon black resulting from spills and leaks, and may also be used to control emissions from storage bins and the bagging operation. Before being vented to the atmosphere, the exhaust air from the vacuum system passes through a cyclone and/or bag filter that removes entrained carbon black (as shown in Figure 8).

Table 30 summarizes the emissions data for product storage and handling operations obtained from the survey of carbon black plants given in Reference 21. Under the assumption that the vacuum cleanup system is employed to control these operations, the data can be equated with emission factors for the vacuum cleanup system vent.[a] The mean emission

Table 30. EMISSIONS DATA FOR PRODUCT STORAGE AND HANDLING[21]

Plant code number	Control device	Carbon black emission factor, g/kg
50-1	Bag filter	0.01
50-2	Bag filter	0.035
50-5	Bag filter	0.02
50-8	Bag filter	0.01
50-9	Bag filter	0.045
50-10	Bag filter	0.02
50-28	Bag filter	0.05
Mean		0.03 ± 58%
Range		0.01 to 0.05

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[a] It is assumed that the additional emissions from this vent as a result of intermittent vacuum cleanup spills and leaks are small compared with those resulting from control of product storage and handling operations. No data are available for the former emissions.

factor for carbon black, the only contaminant in this stream, is 0.03 g/kg. The seven reported values range from 0.01 g/kg to 0.05 g/kg. The 95% confidence limits about the mean are ±58%.

6. Fugitive Emissions

The extremely small particle size and fluffiness of loose carbon black, especially prior to pelletizing, gives rise to numerous sources of fugitive emissions. These include the following:[7]

- Cleaning of clogged screens, production lines, and other process equipment.
- Leaks in the pneumatic system, storage bins, bagging system, and other process equipment. The salty atmosphere of the Gulf Coast area results in severe corrosion problems for the carbon black plants located there. Leaks are also caused by the erosion of conveying equipment by carbon black. They may also result from defective seals on conveying equipment and defective buckets in the elevator.
- Drawing of samples from various points in the production line for testing and quality control.
- Spillage from torn and broken bags during stacking in the warehouse or during loading in box cars.
- Spillage during the loading of hopper cars when the flexible loading pipe is shifted from one compartment to another. Dusting of black also occurs when the loading pipe is inserted into the top of a Sealdbin®.
- Cleaning and sweeping the bottoms of hopper cars.
- Cleaning of process equipment prior to repair work.
- Opening of the rotary valve at the base of the filter, in the event of a fire in a bag filter, to permit removal of the burning and contaminated black. This operation results in atmospheric emissions of carbon black.

Fugitive losses were estimated in Reference 21 to be 0.5 kg/hr for a 4.0×10^4 metric tons/yr carbon black plant. The corresponding emission factor is 0.1 g/kg.

C. ENVIRONMENTAL EFFECTS

1. Definition of a Representative Source

For the purpose of assessing the source severity, a representative carbon black plant is defined to be one producing 5.1×10^4 metric tons/yr of an HAF grade black by the oil furnace process. Although carbon black plants normally produce several different grades of black, the HAF blacks are predominant, accounting for nearly 50% of oil furnace black production (see Figure 22 in Section VI.C.5). In addition, the HAF blacks are intermediate in properties between the smaller particle blacks (SAF, ISAF) and the larger particle blacks (FEF, GPF).

The production rate of 5.1×10^4 metric tons/yr is the arithmetic mean value obtained by dividing the total 1974 production (1.54×10^6 metric tons) by the number of plants (30). In addition, it is assumed that the representative plant is equipped with bag filters on the main process vent, the dryer vent, the pneumatic system vent, and the vacuum cleanup system vent, since this mode of operation predominates in the industry (see Section V.A.). The oil storage tank vents, as well as fugitive emissions, are uncontrolled in all plants.

2. Emission Factors

Emission factors for a representative carbon black plant are presented in Table 31. The values for the main process vent are the measurements made by MRC in the present study. The values for POM and trace elements are totals of the values listed in Tables 24 and 25 for individual POM's and trace elements, respectively. As previously noted, these emission factors correspond to a plant which does not use the process off-gas as fuel in the dryers.

Table 31. EMISSION FACTORS FOR A REPRESENTATIVE CARBON BLACK PLANT

Material emitted	Emission factor,[a] g/kg Main process vent	Dryer vent	Pneumatic system vent	Oil storage tanks	Vacuum cleanup system vent	Fugitive emissions
Criteria pollutants						
Particulate matter[b]	0.11 ± 70%	0.12 ± 89%	0.3 ± 93%		0.03 ± 58%	0.1
Sulfur oxides	_[c]	0.23 ± 60%				
Nitrogen oxides	0.28 ± 1[illegible]	0.60 + 200% - 100%				
Hydrocarbons[d]	50 ± 48%			0.72 ± 10%		
Carbon monoxide	1,400 ± 19%					
Hazardous materials						
Beryllium	2.2×10^{-6} 16%					
Mercury	1.5×10^{-4} + 386% - 100%					
Inert gases						
Nitrogen & argon	9,000 ± 19%	2,200 ± 21%	N.A.[e]			
Oxygen	240 ± 99%	400 ± 65%	N.A.			
Carbon dioxide	700 ± 21%					
Chemical substances						
Hydrogen	120 ± 39%					
Hydrogen sulfide	30 ± 82					
Carbon disulfide	30 ± 76					
Carbonyl sulfide	10 ± 99%					
Carbon black	0.11 ± 70%	0.12 ± 89%	0.3 ± 93%		0.03 ± 58%	0.1
Methane	25 ± 47%					
Acetylene	45 ± 48%					
Ethane	N.A.					
Ethylene	1.6 ± 85%					
Propylene	_[c]					
Propane	0.23 + 109% - 100%					
Isolutane	0.10 ± 80%					
n-Butane	0.27 ± 57%					
n-Pentane	N.A.					
POM (total)[f]	0.002 ± 52%					
Trace elements (total)[g]	<0.25 ± 43					

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[a] Blanks indicate no emissions.

[b] The particulate matter is carbon black.

[c] Not detected at detection limit of 1 ppm.

[d] Total nonmethane hhdrocarbons. The individual hydrocarbon species are listed under chemical substances.

[e] Not available.

[f] Emission factors for individual POM species are given in Table 24, Section IV.B.

[g] Includes beryllium and mercury. Emission factors for individual trace elements are given in Table 25, Section IV.B.

Emission factors given in Table 31 for the dryer vent, the pneumatic system vent, and the vacuum cleanup system vent are mean values of the data given in Tables 27, 28, and 30. The mean value for units with bag filters was used for carbon black emissions from the dryer vent. The emission factor for fugitive emissions is based on the estimate of fugitive emissions given in Reference 21.

The hydrocarbon emission factor for oil storage tanks is that calculated assuming an oil vapor pressure of 0.7 kPa (see Section IV.B.4).

The error bounds given in Table 31 represent 95% confidence limits for the mean emission factors. In the case of fugitive emissions, insufficient information was available to determine either the accuracy or precision of the estimated emission factor. Hence, no error bounds have been assigned to this value.

Emission factors for carbon black plants are independent of plant size since these plants are made up of separate production units, each having multiple reactors which do not vary greatly in size. The emission factors for all sources except the main process vent should also be nearly independent of the type of black produced, since the operating conditions involved do not change with black type. Although carbon black emissions would be expected to increase to some extent with decreasing particle size, such differences are probably small compared with the scatter in emissions data.

3. Source Severity

In order to obtain a quantitative measure of the hazard potential of carbon black production, the source severity, S, is defined as:

$$S = \frac{\bar{\chi}_{max}}{F} \qquad (1)$$

where $\bar{\chi}_{max}$ is the maximum time-averaged ground level concentration of each pollutant emitted from a representative plant, and F is defined as a primary ambient air quality standard for criteria pollutants (particulate, SO_x, NO_x, CO, and hydrocarbons), while for noncriteria pollutants,

$$F \equiv TLV \cdot 8/24 \cdot 0.01$$

The factor 8/24 adjusts the TLV for continuous rather than workday exposure, and the factor of 0.01 accounts for the fact that the general population is a higher risk group than healthy workers.

Thus, the source severity represents the ratio of the maximum mean ground level concentration of a given pollutant to the concentration which constitutes an incipient health hazard.

The maximum ground level concentration, χ_{max}, is calculated according to Gaussian plume dispersion theory:[33]

$$\chi_{max} = \frac{2\,Q}{\pi H^2 e \bar{u}} \qquad (2)$$

where Q = mass emission rate, g/s
π = 3.14
H = effective emission height, m
e = 2.72
$\bar{u}$ = average wind speed, m/s

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[33] Turner, D. B. Workbook of Atmospheric Dispersion Estimates. Public Health Service Publication No. 99-AP-26, U.S. Department of Health, Education, and Welfare, Cincinnati, Ohio, 1969. 84 pp.

Equation 2 yields a value corresponding to an averaging (i.e., sampling) time of approximately 3 minutes.[33,34] For a continuously emitting source, the maximum time-averaged ground level concentration for averaging times between 3 min and 24 hrs can be estimated from the relation:[33,34]

$$\bar{\chi}_{max} = \chi_{max} \left(\frac{t_o}{t}\right)^{0.17} \qquad (3)$$

where t = averaging time
t_o = short-term averaging time (3 min)

In this study, the averaging time, t, for noncriteria pollutants is 24 hours. For criteria pollutants, the averaging times are those used in the definition of the primary ambient air quality standards. The only exception is NO_x, for which the primary standard averaging time is 1 year. Since Equation 3 is not valid for averaging times of this magnitude, the calculation of $\bar{\chi}_{max}$ for NO_x is based on Equation 5.13 of Reference 33 which estimates the annual average ground level concentration.

Insertion of the national average wind speed of 4.5 m/s into the above equations leads to the source severity equations listed in Table 32. The emission heights used in the calculations are given in Table 33. The heights for the oil storage tanks and fugitive emissions were assumed. The others were obtained by averaging the operating plant data given in Reference 21. The emission rates, Q, were calculated using the emission factors listed in Tables 24, 25, and

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[34] Nonhebel, G. Recommendations on Heights for New Industrial Chimneys. Journal of the Institute of Fuel. 33:479-511, 1960.

Table 32. SOURCE SEVERITY FACTOR EQUATIONS

Pollutant	S, dimensionless
Particulate matter	$70\ QH^{-2}$
SO_x	$50\ QH^{-2}$
NO_x	$315\ QH^{-2.1}$
Hydrocarbons	$162.5\ QH^{-2}$
Carbon monoxide	$0.78\ QH^{-2}$
All others	$5.5\ QH^{-2}(TLV)^{-1}$

Q = emission rate, g/s
H = effective emission height, m
TLV = threshold limit value, g/m^3

Table 33. EMISSION HEIGHTS FOR REPRESENTATIVE SOURCE

Source of emissions	Emission height, m
Main process vent	25
Dryer vent	20
Pneumatic system vent	25
Oil storage tanks	15
Vacuum cleanup system vent	20
Fugitive emissions	3.1

31. The resulting values of the maximum time-averaged ground level concentration, $\bar{\chi}_{max}$, are presented in Table 34, while the source severities are given in Tables 35, 36, and 37. In arriving at these results, it was assumed that Gaussian plume dispersion theory was equally valid for all emissions, irrespective of their chemical, physical, or topological characteristics. In addition, plume rise was

Table 34. MAXIMUM TIME-AVERAGED GROUND LEVEL CONCENTRATION FOR A REPRESENTATIVE CARBON BLACK PLANT

	$\bar{\chi}_{max}$,[a] μg/m^3					
Material emitted	Main process vent	Dryer vent	Pneumatic system vent	Oil storage tanks	Vacuum cleanup system vent	Fugitive emissions
Criteria pollutants[b]						
Particulate matter[b]	5.2	8.8	13.7		2.2	307
Sulfur oxides	0.0[c]	16.9				
Nitrogen oxides	13.2	44.9				
Hydrocarbons[d]	2,360			9.2		
Carbon monoxide	66,110					
Hazardous materials						
Beryllium	1.7×10^{-4}					
Mercury	7.1×10^{-3}					
Chemical substances						
Hydrogen sulfide	990					
Carbon disulfide	1,510					
Carbonyl sulfide	410					
Carbon black	5.2	8.8	13.7		2.2	307
Methane	1,180					
Acetylene	2,220					
Ethylene	76					
Ethane	0.0[c]					
Propylene	0.0[c]					
Propane	9.4					
Isobutane	4.7					
n-Butane	12.7					
n-Pentane	0.0[c]					
POM (total)	0.094					
Trace elements[e] (total)	<11.8					

[a] Blanks indicate no emissions. Averaging times for criteria pollutants are those specified in the primary ambient air quality standards. For noncriteria pollutants, the averaging time is 24 hours.

[b] The particulate matter is carbon black.

[c] Not detected in process vent gas at detection limit of 1 ppm.

[d] Total nonmethane hydrocarbons; individual hydrocarbon species are listed under chemical substances.

[e] Includes beryllium and mercury.

Table 35. SOURCE SEVERITIES FOR A REPRESENTATIVE CARBON BLACK PLANT

	Source severity[a]					
Material emitted	Main process vent	Dryer vent	Pneumatic system vent	Oil storage tanks	Vacuum cleanup system vent	Fugitive emissions
Criteria pollutants						
Particulate matter[b]	0.02	0.034	0.053		0.008	1.2
Sulfur oxides	0.0[c]	0.046				
Nitrogen oxides	0.16	0.58				
Hydrocarbons[d]	21			0.84		
Carbon monoxide	1.8					
Hazardous materials						
Beryllium	0.028					
Mercury	0.042					
Chemical substances						
Hydrogen sulfide	20					
Carbon disulfide	7.6					
Carbonyl sulfide	2.1					
Methane	–[e]					
Acetylene	–[e]					
Ethylene	–[e]					
Ethane	–[e]					
Propylene	0.0[c]					
Propane	–[e]					
Isobutane	0.001					
n-Butane	0.003					
n-Pentane	0.0[c]					
Carbon black[f]	0.45	0.76	1.2		0.34	27
POM (total)[g]	2.1					
Trace elements[g,h] (total)	<2.7					

[a] Calculated assuming no plume rise. If plume rise is included in the calculations, severities of emissions from the main process vent are reduced by a factor of 0.2; severities of emissions from the dryer vent are reduced by a factor of 0.6; severities of other emissions are unchanged. Blanks indicate no emissions.

[b] The particulate matter is carbon black. Source severities were computed using the severity equation for particulate matter.

[c] Not detected at detection limit of 1 ppm.

[d] Total nonmethane hydrocarbon severities were calculated using the severity equation for hydrocarbons.

[e] Classified as "inert" gas, i.e., simple asphyxiant. TLV has not been established.

[f] Severities calculated using TLV of 0.0035 g/m^3 for carbon black.

[g] Source severities for individual POM's and trace elements are given in Tables 36 and 37.

[h] Includes beryllium and mercury.

Table 36. SOURCE SEVERITIES FOR POLYCYCLIC ORGANIC COMPOUNDS IN MAIN PROCESS VENT GAS

Compound	Carcinogenicity indicator[a]	Source severity[b]
Acenaphthylene	-	0.057
Anthracene/phenanthrene	-	0.005
Benzo[c]phenanthrene	+++	<0.028
Benzofluoroanthenes	++	0.43
Benzo[ghi]fluoranthene	-	0.0028
Benzo[ghi]perylene/anthanthrene	-	0.0016
Benzopyrenes & perylene	+++	0.42
Chrysene/benzo[a]anthracene	±	0.00062
Dibenzanthracenes	+	<0.028
Dibenzo[c,g]carbazole	+++	<0.028
Dibenzopyrenes	+++	<0.028
Dibenzothiophene	-	0.001
Dimethylanthracenes/phenanthrenes	-	0.01
7,12-Dimethylbenz[a]anthracene	++++	0.99
Fluoranthene	-	0.0042
Indeno[1,2,3-cd]pyrene	+	<0.028
Methylanthracenes/phenanthrenes	-	0.0071
Methylcholanthrene	++++	<0.028
Methylfluoranthene/pyrene	-	0.0016
Pyrene	-	0.035

[a] The carcinogenicity indicators are defined as follows:[35]
- not carcinogenic
± uncertain or weakly carcinogenic
+ carcinogenic
++, +++, ++++ strongly carcinogenic

[b] Calculated assuming no plume rise. If plume rise is included in the calculation, the severities are reduced by a factor of 0.2.

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[35] Particulate Polycyclic Organic Matter. National Academy of Sciences, Washington, D.C., 1972. 361 pp.

Table 37. SOURCE SEVERITIES FOR TRACE ELEMENTS IN MAIN PROCESS VENT GAS

Element	Source Severity[a]
Aluminum	Indeterminate[b]
Antimony	0.00071
Arsenic	0.0010
Barium	<0.063[c]
Beryllium	<0.028
Bismuth	Indeterminate[b]
Boron	Indeterminate[b]
Bromine	0.00018
Cadmium	0.0040
Calcium	Indeterminate[b]
Cerium	Indeterminate[b]
Cesium	Indeterminate[b]
Chlorine	<0.028[c]
Chromium	<0.011[c]
Cobalt	0.016
Copper	<0.71[c]
Dysprosium	Indeterminate[b]
Erbium	Indeterminate[b]
Europium	Indeterminate[b]
Fluorine	<0.014[c]
Gadolinium	Indeterminate[b]
Gallium	Indeterminate[b]
Germanium	Indeterminate[b]
Gold	Indeterminate[b]
Hafnium	<0.00045
Holmium	Indeterminate[b]
Iodine	<0.000071
Iridium	Indeterminate[b]
Iron	Indeterminate[b]
Lanthanum	Indeterminate[b]
Lead	<0.14[c]
Lithium	Indeterminate[b]
Lutecium	Indeterminate[b]
Magnesium	Indeterminate[b]
Manganese	<0.00037[c]
Mercury	0.042
Molybdenum	<0.00039[c]
Neodymium	Indeterminate[b]
Nickel	0.18
Niobium	Indeterminate[b]
Osmium	Indeterminate[b]
Palladium	Indeterminate[b]
Phosphorus	<1.4[c]
Platinum	<0.053

Table 37 (continued). SOURCE SEVERITIES FOR TRACE ELEMENTS IN MAIN PROCESS VENT GAS

Element	Source Severity
Potassium	Indeterminate[b]
Praseodymium	Indeterminate[b]
Rhodium	<0.00028
Rubidium	Indeterminate[b]
Samarium	Indeterminate[b]
Scandium	Indeterminate[b]
Selenium	<0.00011
Silicon	<0.028[c]
Sodium	Indeterminate[b]
Strontium	Indeterminate[b]
Tantalum	Indeterminate[b]
Terbium	Indeterminate[b]
Tellurium	<0.00042
Thallium	<0.0010
Thorium	Indeterminate[b]
Thulium	Indeterminate[b]
Tin	<0.0092[c]
Titanium	Indeterminate[b]
Tungsten	<0.00035
Uranium	<0.00057
Vanadium	<0.00037[c]
Ytterbium	Indeterminate[b]
Yttrium	<0.00014[c]
Zinc	Indeterminate[b]
Zirconium	<0.00017[c]

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[a] Calculated assuming no plume rise. If plume rise is included in the calculation, the severities are reduced by a factor of 0.2.

[b] Threshold limit value has not been established.

[c] Value reported as upper bound since significant amount of material was found in blank sampling run (see Appendix F).

not taken into account in the calculations, i.e., the effective emission height was equated with the physical stack height. It is shown in Appendix C that if plume rise is taken into account, the values of $\bar{\chi}_{max}$ and source severity for the main process vent gas are decreased by a multiplicative factor of 0.2, while those for the dryer vent are decreased by a multiplicative factor of 0.6. The values for the other emission points are unchanged.

As indicated in Table 35, source severities for carbon black were computed using both the primary ambient air quality standard for particulate matter and the TLV of 0.0035 g/m^3 for carbon black. Since carbon black is not classified as a toxic substance[10], it should properly be assigned the TLV of 0.01 g/m^3 for "nuisance" particles. However, the lower TLV is being retained for "housekeeping" purposes by the American Conference of Governmental Industrial Hygienists.[10] If the TLV for nuisance particles were used, the source severities listed in Table 35 under "carbon black" would be decreased by a multiplicative factor of 0.35. From a human health standpoint, the severities listed in Table 35 for particulate matter are more appropriate than those based on the TLV for either carbon black or nuisance particles. The latter two values are derived from considerations other than health effects.

Extensive small animal and laboratory tests with carbon black have demonstrated that polycyclic organic material absorbed on the black is not released *in vivo* and does not represent a health hazard.[9,36-40] Hence, it is important

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[36] Neal, J., M. Thornton, and C. A. Nau. Polycyclic Hydrocarbon Elution from Carbon Black or Rubber Products. Archives of Environmental Health, 4:46-54, 1962.

(continued)

to determine how much of the total POM emitted from the main process vent is associated with the carbon black in the vent gas. Using the data obtained in this study on the POM content of carbon black (see Table 6, Section III.A), it is found that less than 1% of the POM in the vent gas is adsorbed on the carbon black.[a] Thus, essentially all of the POM is emitted in vapor form which is capable of being absorbed by living tissue. A similar calculation yields an identical result for trace elements.

From Table 36, it is seen that only three POM's have severities exceeding 0.1: 7,12-dimethylbenz[a]anthracene, benzopyrenes/perylene, and benzofluoranthenes, all of which are

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[a] For example, consider pyrene. From Table 24, the total emission factor for pyrene is 5.0×10^{-4} g/kg. From Table 6, the concentration in N-330 black is 27 ppm, or 27×10^{-6} g pyrene/g carbon black. The emission factor for carbon black is 0.11 g/kg from Table 31. Hence, the pyrene emitted with the carbon black is given by

$$\frac{0.11 \text{ g black emitted}}{\text{kg product}} \times 27 \times 10^{-6} \frac{\text{g pyrene}}{\text{g black}} = 3.0 \times 10^{-6} \text{ g/kg}$$

The percentage of total pyrene emissions which is adsorbed on carbon black is thus

$$\frac{3.0 \times 10^{-6}}{5.0 \times 10^{-4}} = 0.6\%$$

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[37] Nau, C. A., J. Neal, and V. Stembridge. A Study of the Physiological Effects of Carbon Black. I: Ingestion. Archives of Industrial Hygiene, 17:21-28, 1958.

[38] Nau, C. A., J. Neal, and V. Stembridge. A Study of the Physiological Effects of Carbon Black. II: Skin Contact. Archives of Industrial Hygiene, 18:511-520, 1958.

[39] Nau, C. A., J. Neal, and V. Stembridge. A Study of the Physiological Effects of Carbon Black. III: Absorption and Elution Potentials. Subcutaneous Injections. Archives of Industrial Hygiene, 20:512-533, 1960.

[40] Nau, C. A., J. Neal, V. Stembridge, and R. N. Cooley. Physiological Effects of Carbon Black. IV: Inhalation. Archives of Environmental Health, 44:15-431, 1962.

strongly carcinogenic. However, if plume rise were taken into account, the severities of the latter two species would be less than 0.1.

From Table 37, it can be seen that for most trace elements the source severity is either indeterminant (because no TLV has been established) or is determined only to within an upper bound due to limitations of the sampling and analytical procedures. The severity of only one element, nickel, definitely exceeds 0.1. The severities of copper, lead, and phosphorus may exceed 0.1 since the upper bounds determined for these elements are greater than 0.1. If plume rise were taken into account, the severities of both nickel and lead would be less than 0.1.

All four of the above elements were detected in significant amounts in either the oil feedstock or the process quench water, as shown in Table 38. Clearly, copper, lead, and nickel originate from the feedstock, while phosphorus originates from both the feedstock and the quench water.

Table 38. CONCENTRATIONS OF HIGH SEVERITY TRACE ELEMENTS IN FEEDSTOCK AND QUENCH WATER

Element	Source severity	Concentration in feedstock, ppm	Concentration in quench water, ppm
Copper	<0.71	1.6	0.017
Lead	<0.14	0.30	0.001
Nickel	0.18	5.5	<0.001
Phosphorus	<1.4	4.3	3.0

4. Source Severity Distributions

Source severity distributions are presented in Figures 10 through 13 for carbon monoxide, hydrogen sulfide, sulfur

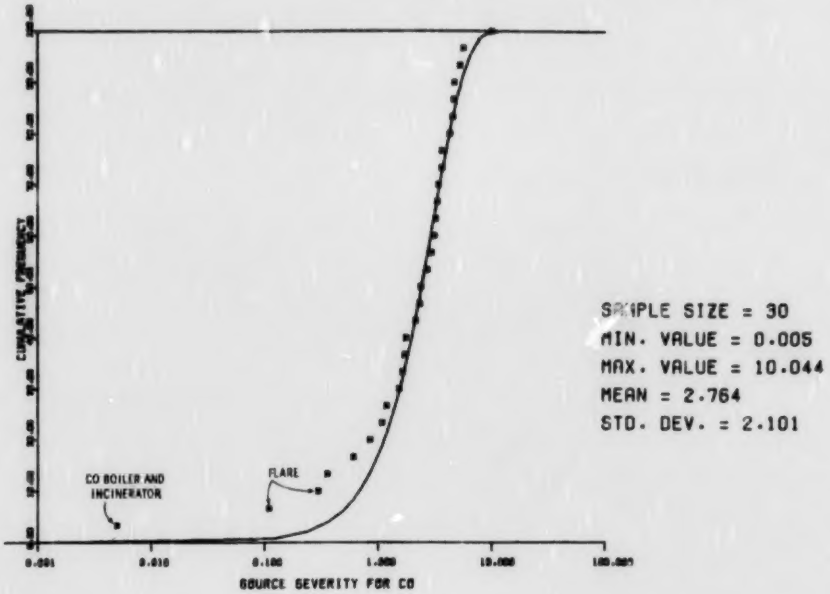


Figure 10. Deterministic source severity distribution for carbon monoxide emissions from main process vent

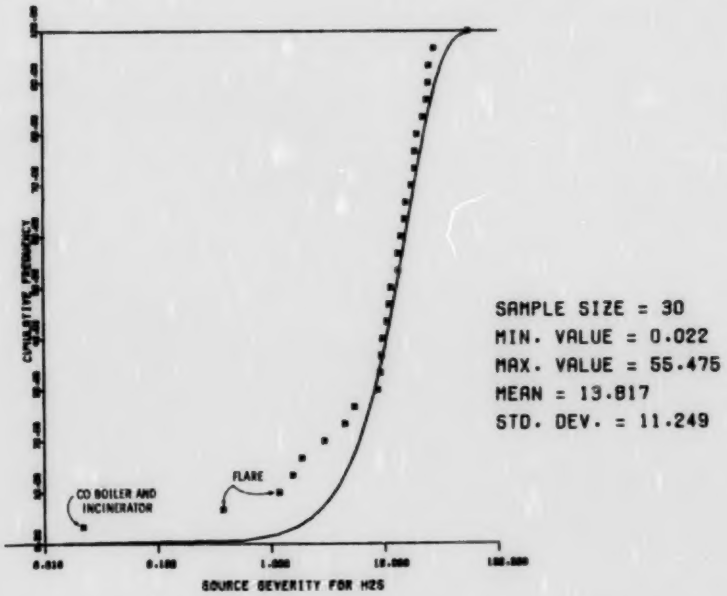
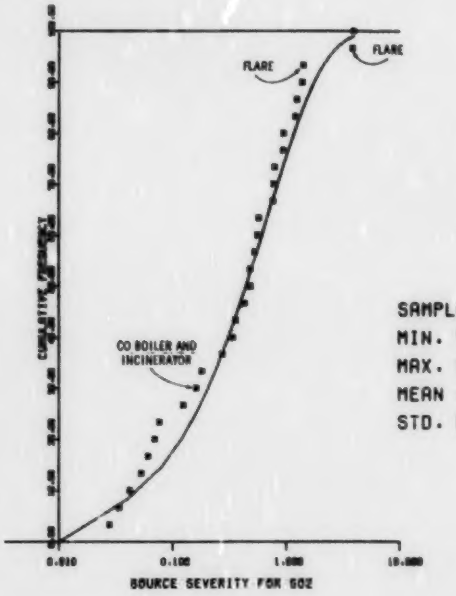
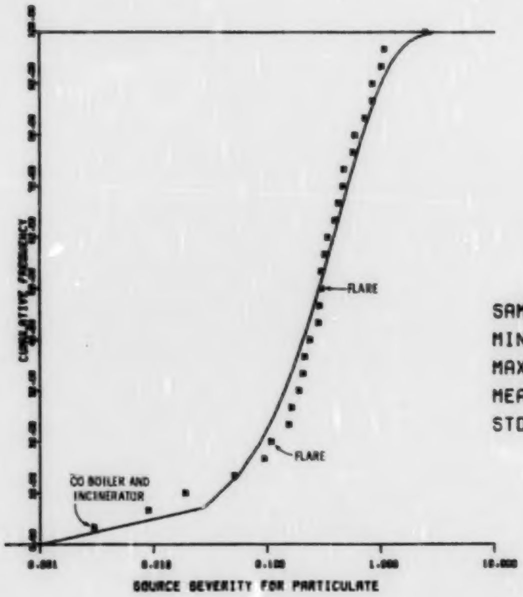


Figure 11. Deterministic source severity distribution for hydrogen sulfide emissions from main process vent



SAMPLE SIZE = 30
MIN. VALUE = 0.028
MAX. VALUE = 3.972
MEAN = 0.742
STD. DEV. = 0.966

Figure 12. Deterministic source severity distribution for sulfur oxide emissions from main process vent



SAMPLE SIZE = 30
MIN. VALUE = 0.003
MAX. VALUE = 2.466
MEAN = 0.438
STD. DEV. = 0.480

Figure 13. Deterministic source severity distribution for particulate emissions from main process vent

oxides and particulate emissions from the main process vent. These distributions are based on data from the survey of operating plants given in Reference 21. Simulated source severity distributions for other emissions (for which data were not given in Reference 21) are presented in Appendix G.

The ordinate in Figures 10 through 13, labeled "cumulative frequency," should be interpreted as the percentage of carbon black plants having source severities less than the corresponding value on the abscissa. For example, from Figure 10, approximately 20% of carbon black plants have carbon monoxide severities less than 1.0. The solid curves in the figures were drawn by fitting a Weibull frequency distribution to the data points.[41]

The points corresponding to the three plants which burn the main process vent gas are indicated on the graphs. The following assumptions were made in calculating these points:

- For the carbon monoxide boiler-thermal incinerator combination, combustion efficiencies of 99% for carbon monoxide and hydrogen sulfide, and 95% for particulate matter, were assumed.
- For the flares, 90% combustion efficiency for carbon monoxide and hydrogen sulfide, and 20% for particulate matter were assumed as in Reference 21.
- The particulate severities were computed using the primary ambient air quality standard for particulate matter (as opposed to the TLV for carbon black or for nuisance particles).

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[41] Eimutis, E. C., B. J. Holmes, and L. B. Mote. Source Assessment: Severity of Stationary Air Pollution Sources - A Simulation Approach. EPA-600/2-76-032e. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, July 1976. 119 pp.

In all other cases, missing data were equated with the mean values of the existing data.

It should be noted that field measurements made in the present study indicate a carbon monoxide combustion efficiency in excess of 99.9% in the flare. This value would yield carbon monoxide severities two orders of magnitude lower than those given in Figure 10 for the plants which flare the vent gas.

It will be noted that the mean severities given in Figures 10 through 13 are not identical to the severities for a representative plant listed in Table 35. There are two reasons for the differences: (1) the mean emission factors for the data given in Reference 21 are not identical to the emission factors for the representative plant (Table 31), and (2) source severity is a nonlinear function of the two variables, emission rate and emission height, both of which vary from plant to plant. Therefore, the mean severity is not equal to the severity calculated using mean emission rate and mean emission height.

5. National and State Emissions Burdens

The mass emissions of criteria pollutants (particulate, SO_x, NO_x, carbon monoxide, and hydrocarbons) resulting from carbon black production were calculated using the emission factors from Table 31 and the production data from Table 21. The appropriate emission factor was multiplied by the annual production nationwide and by that for the states of Texas and Louisiana, in which the carbon black plants are concentrated. The total annual mass emissions of criteria pollutants from all sources nationwide and from sources within the states of Texas and Louisiana were obtained from

Reference 42. The percentages of the total emissions resulting from carbon black manufacture were computed using these values and are presented in Table 39.

Table 39. CONTRIBUTION TO TOTAL EMISSIONS OF CRITERIA POLLUTANTS BY CARBON BLACK INDUSTRY

Material emitted	Industry contribution, %		
	Nationwide	Texas	Louisiana
Particulate matter	0.01	0.08	0.09
Sulfur oxides	0.001	0.02	0.07
Nitrogen oxides	0.008	0.04	0.12
Hydrocarbons	0.31	1.5	1.4
Carbon monoxide	2.3	13	13

6. Affected Population

A measure of the population which is exposed to a high contaminant concentration due to a representative carbon black plant can be obtained as follows. The values of x for which

$$\frac{\bar{\chi}(x)}{F} = m \tag{4}$$

for

$$m = 0.1 \text{ and } 1.0$$

are determined by iteration. The value of $\bar{\chi}(x)$, the annual mean ground level concentration, is computed from the equation:[33]

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[42] 1972 National Emissions Report. EPA-450/2-74-012, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 1974. 422 pp.

$$\bar{\chi}(x) = \frac{2.03\ Q}{\sigma_z \bar{u} x} \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \qquad (5)$$

where Q = emission rate, g/s

H = effective emission height, m

x = downwind distance from source, m

$\bar{u}$ = average wind speed, 4.5 m/s

σ_z = vertical dispersion coefficient, m

For atmospheric stability class C (neutral conditions), σ_z is given by:[43]

$$\sigma_z = 0.113\ (x^{0.911}) \qquad (6)$$

The affected area, A(km^2), is then computed as

$$A = \pi(x_2{}^2 - x_1{}^2) \qquad (7)$$

where x_1 and x_2 are the two roots of Equation 4 for a given value of m.

The capacity-weighted mean population density, $\bar{D}_p$, is calculated as follows:

$$\bar{D}_p = \frac{\sum_i C_i D_{p_i}}{\sum_i C_i}\ \text{, persons/km}^2 \qquad (8)$$

where C_i = production capacity of plant i

D_{p_i} = county population density for plant i

The product $A \cdot \bar{D}_p$ is designated the "affected population."

The affected population was computed for each compound and each emission point for which the source severity for a representative plant exceeds 0.1. The results are presented in Table 40.

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[43] Eimutis, E. C., and M. G. Konicek. Derivations of Continuous Functions for the Lateral and Vertical Atmospheric Dispersion Coefficients. Atmospheric Environment, 6:859-863, 1972.

The mean population density (from Equation 8) for carbon black plants is 57 persons per square kilometer. The largest value of affected population results from hydrogen sulfide emissions from the main process vent: 11,000 persons where $\overline{\chi}/F \geq 0.1$ and 1,000 persons where $\overline{\chi}/F \geq 1.0$.

7. Growth Factor

In 1974, 1.54×10^6 metric tons of carbon black was produced in the United States.[26] As discussed in Section VI, production in 1980 is expected to total from 1.73×10^6 to 1.79×10^6 metric tons. Thus, taking an average value of 1.76×10^6 metric tons for 1980 production, and assuming that the same level of control technology exists in 1980 as existed in 1974, the emissions from the carbon black industry will increase by 14% over that period, i.e.:

$$\frac{\text{Emissions in 1980}}{\text{Emissions in 1974}} = \frac{1.76 \times 10^6}{1.54 \times 10^6} = 1.14$$

Table 40. AFFECTED POPULATION

Emitted species	Emission point	No. of persons where $\overline{\chi}/F \geq 1.0$	No. of persons where $\overline{\chi}/F \geq 0.1$
Particulate matter	Fugitive emissions	0	10
Nitrogen oxides	Main process vent	0	40
Nitrogen oxides	Dryer vent	0	100
Hydrocarbons	Main process vent	700	8,000
Hydrocarbons	Storage tanks	0	80
Carbon monoxide	Main process vent	50	800
Hydrogen sulfide	Main process vent	1,000	11,000
Carbon disulfide	Main process vent	300	4,000
Carbonyl sulfide	Main process vent	70	1,000
Carbon black	Main process vent	0	200
Carbon black	Dryer vent	0	200
Carbon black	Pneumatic system vent	20	500
Carbon black	Vacuum cleanup vent	0	40
Carbon black	Fugitive emissions	20	170
Lead	Main process vent	0	40
Nickel	Main process vent	0	60
Copper	Main process vent	0	300
Phosphorous	Main process vent	40	700
Benzofluoroanthenes	Main process vent	0	200
Benzopyrenes	Main process vent	0	200
7,12-Dimethylbenz[a]anthracene	Main process vent	20	500

SECTION V

CONTROL TECHNOLOGY

A. STATE OF THE ART

1. Primary Recovery Device

The application of emissions control technology in furnace black plants is summarized in Table 41. It can be seen that all but four of the 30 plants covered in the Houdry survey[21] employ bag filters on all process trains to recover carbon black from the reactor effluent. Electrostatic precipitators and cyclones, which predated the use of bag filters, are still in operation in some plants as supplementary recovery devices. However, the trend is toward the use of bag filters as the sole means of product recovery.

Bag filters in carbon black plants reportedly have recovery efficiencies of up to 99.95%;[21] 99.99% recovery was measured in the field sampling program conducted in the present study. Since their principal function is product recovery rather than emissions control, bag filters were discussed in detail in Section III.

Four plants still employ scrubbers on at least one process train. These units have efficiencies of only 90% to 95%, and for this reason they are being phased out of product recovery service.[21]

Table 41. SUMMARY OF EMISSION CONTROL DEVICES IN FURNACE BLACK PLANTS[21]

Control device type		Number of plants
Primary recovery device		
Bag filter only - all process trains		16
Cyclone & bag filter		4
Electrostatic precipitator & cyclone & bag filter	one or more process trains	6
Electrostatic precipitator & cyclone & scrubber		4
Combustion device for process vent gas		
None		27
Flare		2
CO boiler & incinerator		1
CO boiler only		0
Incinerator only		0
Dryer vent control device		
Bag filter		19
Scrubber		6
None		5
Vacuum cleanup system		20

2. Combustion Devices

It can be seen from Table 41 that most carbon black plants vent the main process off-gas directly to the atmosphere after product recovery. Two plants flare the off-gas and report "about 90% combustion."[21] However, the degree of combustion attainable by this method depends on the heating value of the vent gas. Thus, the removal efficiency for combustible gases is estimated to range from 75% to 80% for the production of low yield blacks and up to 95% for high yield blacks.[21] It is estimated that 20% to 30% of the vented carbon black is burned.[21]

Field sampling data obtained in the present study indicate a much higher flare removal efficiency for carbon monoxide than the above estimates. The concentration of carbon monoxide in the flare off-gas was measured at 50 ppm, corresponding to a combustion efficiency greater than 99.9% in the flare. (Details of the experimental procedure are given in Appendix H).

One other plant in the United States burns the main process vent gas, utilizing a carbon monoxide boiler and thermal incinerator in combination. About 60% of the vent gas is burned with supplemental fuel in the carbon monoxide boiler to provide the process steam requirements for the plant. Another 10% of the vent gas is used in the dryers, and the remaining 30% is disposed of in the incinerator.

A typical carbon monoxide boiler-thermal incinerator control system is shown schematically in Figure 14. This system differs from the one actually in use in that provision is made for energy recovery in the incinerator by preheating the feed streams. The supplemental fuel requirement of the incinerator is thereby minimized. Also, in Figure 14 it is assumed that none of the vent gas is utilized in the process dryers. A material balance for this system, based on the process vent gas (stream 11) of Table 19, is presented in Table 42. Complete combustion of carbon monoxide, sulfur compounds, hydrocarbons, and particulate matter is assumed in the material balance.

Both the carbon monoxide boiler and the thermal incinerator are designed to operate at a temperature of 980°C in the combustion zone with excess air equivalent to 4 mole percent oxygen in the stack gas. Based on a heating value of 1.49 MJ/m^3 for the process vent gas, the energy recovery in the incinerator is sufficient to maintain the required operating temperature without any additional fuel except for the pilots.

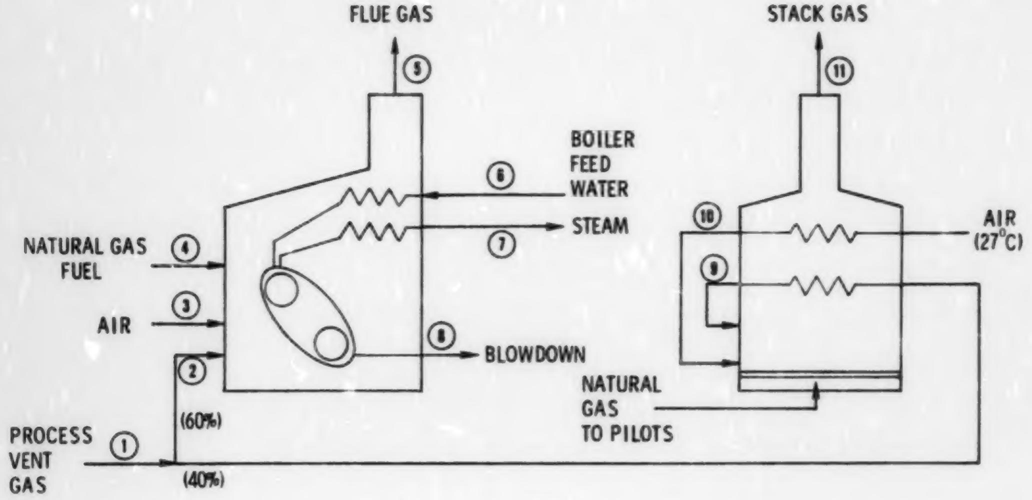
FLUE GAS
⑤
STACK GAS
⑪
BOILER
FEED
WATER
⑥
STEAM
⑦
⑩
AIR
(27°C)
NATURAL GAS
FUEL
④
⑨
AIR
③
⑧
BLOWDOWN
②
NATURAL
GAS
TO PILOTS
(60%)
PROCESS
VENT
GAS
①
(40%)

Figure 14. CO boiler-thermal incinerator system for carbon black plant[21]

The following problems are associated with the use of carbon monoxide boilers in carbon black plants:[21]

- Process vent gas is available only at low pressure and is corrosive. Hence, a large investment is required for blowers, large diameter pipes and valves, control equipment, and burning equipment.

- Because of the low heating value of the process vent gas (1.12 to 1.86 MJ/m^3), up to 35% of the total heating value must be added as supplemental fuel in order to achieve complete combustion.

Table 42. MATERIAL BALANCE FOR CO BOILER-THERMAL INCINERATOR CONTROL SYSTEM[21]

Stream no.:	1	2	3	4	5	6
Description:	Process vent gas	Vent gas to CO boiler	Air to CO boiler	Natural gas to CO boiler	Flue gas from boiler	Boiler feed water
Temperature, °C:	232	232	27	27	400	116
Gage pressure, kPa:[a]						
Component	Flow rates,[b] kg/hr					
Hydrogen	563	338				
Carbon dioxide	3,518	2,111			10,002	
Carbon monoxide	7,029	4,217				
Hydrogen sulfide	66	40				
Sulfur oxides	0.6	0.4			158	
Methane	145	87		185		
Acetylene	174	104				
Ethane				40		
Carbon black	11	6.6				
Nitrogen	41,221	24,733	30,428	19	55,182	
Oxygen	739	443	9,224		2,919	
Water	36,465	21,879	432		26,074	25,973
Nitrogen oxides	8.2	4.9			11	
Carbon disulfide	66	40				
Carbonyl sulfide	23	14				
TOTALS	90,029	54,018	40,084	244	94,346	25,973

[a] Except as indicated, all streams are at low pressure, i.e., atmospheric or slightly above.

[b] Blanks indicate no mass flow of component.

Table 42 (continued). MATERIAL BALANCE FOR CO BOILER-THERMAL INCINERATOR CONTROL SYSTEM[21]

Stream no.:	7	8	9	10	11
Description:	Steam	Boiler blowdown	Vent gas to incinerator	Air to incinerator	Incinerator stack gas
Temperature, °C:	400	238	232	27	870
Gage pressure, kPa:[a]	3,103				
Component	Flow rates,[b] kg/hr				
Hydrogen			225		
Carbon dioxide			1,407		6,251
Carbon monoxide			2,812		
Hydrogen sulfide			26		
Sulfur oxides			0.2		105
Methane			58		
Acetylene			70		
Ethane					
Carbon black			4.4		
Nitrogen			16,488	17,919	34,407
Oxygen			296	5,428	1,819
Water	24,727	1,246	14,586	253	17,023
Nitrogen oxides			3.2		6
Carbon disulfide			26		
Carbonyl sulfide			9		
TOTALS	24,727	1,246	36,011	23,600	59,611

[a] Except as indicated, all streams are at low pressure, i.e., atmospheric or slightly above.

[b] Blanks indicate no mass flow of component.

In addition to the above problems, combustion of the process vent gas results in increased emissions of sulfur oxides and nitrogen oxides. Removal of these contaminants would be difficult and expensive due to their low concentrations (0.02% to 0.17% by volume, dry basis).[21] Based on the material balance in Table 42, a stack height of 41 m,[21] and no plume rise, the source severities for the carbon monoxide boiler-incinerator system in a 5.1×10^4 metric tons/yr plant (the representative plant size) would be 2.8 for SO_x and 0.76 for NO_x. The SO_x severity which results from combustion of the vent gas depends on the amount of sulfur-containing compounds in the vent gas, as well as on the emission height of the combusted gas. The emission height is affected because combustion increases the temperature of the vent gas, which results in greater plume rise. The SO_x severity resulting from combustion was also calculated for a vent gas having the composition listed in Table 26 (Section IV.B.1). This composition was measured by MRC in the present study, and was used as the basis for the source severities for the representative plant listed in Table 35 (Section IV.C.3). This vent gas corresponds to a feedstock having a relatively high (3.7%) sulfur content. The following assumptions were made:

- Complete combustion of all sulfur compounds in the vent gas
- A stack height of 25 m, the same as that for the main process vent in the representative plant
- Production rate of 5.1×10^4 metric tons/yr, the same as that for the representative plant
- No plume rise

The resulting SO_x severity was 15. Inclusion of plume rise in the calculation gave a severity of 2.3. Thus, control of hydrogen sulfide, carbonyl sulfide, and carbon disulfide (uncontrolled severities of 20, 2.1 and 7.6, respectively, neglecting plume rise; uncontrolled severities of 4.0, 0.4 and 1.5, respectively, including plume rise) is achieved at the expense of a relatively high SO_x severity.

3. Dryer Vent Gas Control

Nearly two-thirds of the furnace black plants employ bag filters to remove entrained carbon black from the direct-fired dryer vent gas stream. The control efficiency of these devices is 99.8% to 99.95%.[21]

One manufacturer uses a three-stage water scrubbing system in its plants, in which the dryer vent gas is sucked into a tangential entry, vertical, cylindrical scrubber by means of a blower located downstream of the scrubber. The discharge from the blower is fed to a venturi scrubber which vents through a cyclone separator to the atmosphere. Water is sprayed into the blower inlet as well as the two scrubbers to provide three scrubbing stages. Slurry collected from the cylindrical scrubber and cyclone separator is recycled to the scrubber sprays and reactor quench streams. All of the carbon black recovered from the dryer vent gas is thus return to the main process sequence.

Impinger-reactor scrubbers, which are described in Reference 44, are in use in at least one carbon black plant. The particulate removal efficiency attained by the units in this installation is 92.8%, with an estimated availability of 80%.[44]

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[44] Hesketh, H. E. Scrubbing with an Impinger Reactor. In: Proceedings of the Second National Conference on Energy and the Environment, College Corner, Ohio, November 13-15, 1974. pp. 174-176.

4. Other Control Devices

Carbon black is recovered from the pneumatic transport system by means of a bag filter and/or a cyclone. When only a cyclone is used, the exhaust gas is recycled to the product recovery bag filters to form a closed system. When a bag filter is used with the cyclone, the exhaust gas is vented to the atmosphere.

Two-thirds of the furnace black plants incorporate a plant-wide vacuum cleanup system such as the one described in Section III.B.5. This system is used to pick up loose carbon black resulting from leaks and spills. It can also be used to control emissions from the carbon black storage bins and from the bagging system. Some plants employ separate bag filters on the storage bin vents to control carbon black emissions.

The oil feedstock storage tanks are not equipped with control devices. Although conservation vents or floating roof tanks could be used for control, all feedstock storage tanks meet EPA New Source Performance Standards for this type of emission point (personal communication, C. B. Beck, Cabot Corporation, Pampa, Texas, 26 February 1976).

One carbon black plant reportedly employs a fluid bed incinerator to dispose of waste sludge.[45] Solid waste incinerators in two plants are reported in the National Emission Data System point source listing. The sludge burned in these units originates from scrubbers and/or washdown of carbon black spills. Liquid waste from these operations is usually recycled via the quench water streams or allowed to evaporate in settling ponds. The sludge from the settling ponds, which ranges from 0 to 20 g/kg of product, is normally used as landfill rather than being incinerated.[21] Other solid waste from carbon black operations consists of used filter bags (0.15 to 0.25 g/kg product) and used furnace refractory bricks (0.35 to 0.75 g/kg product).[21]

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[45] Wall, C. J., J. T. Graves, and E. J. Roberts. How to Burn Salty Sludges. Chemical Engineering, 82:77-82, 1975.

Estimated emission factors for solid waste incineration in carbon black plants, based on emission rates obtained from the National Emission Data System, are given in Table 43.

Table 43. ESTIMATED EMISSION FACTORS FOR SOLID WASTE INCINERATORS IN CARBON BLACK PLANTS

Material emitted	Emission factor, g/kg
Particulate matter	0.12
SO_x	0.01
NO_x	0.04
Hydrocarbons	0.01
Carbon monoxide	0.01

B. FUTURE CONSIDERATIONS

1. Combustion Devices for Existing Plants

a. Thermal Incinerator - The principal source of atmospheric emissions from carbon black plants is the main process vent gas. Hence, the implementation of combustion devices to control these emissions will play a central role in future control strategy. Since most existing carbon black plants are not designed for steam-driven operation, the most effective combustion device for these plants would probably be a flare or a thermal incinerator of the type discussed previously in Section V.A.2 and illustrated in Figure 14. This incinerator minimizes supplementary fuel consumption by recovering the heat of combustion via heat exchange with the air and vent gas feed streams.

Table 44 presents a material balance for a thermal incinerator treating the vent gas stream (stream 11) of Table 19. Complete combustion of all combustible material is assumed. Based on this material balance, a stack height of 41 m,[21] and no plume rise, the source severities for SO_x and NO_x for a 5.1 x 10^4 metric tons/yr plant (the representative plant size) would be 2.6 and 0.64, respectively.

b. Catalytic Incinerator - Catalytic incineration is an alternative to thermal incineration with feed preheat. A catalytic incinerator is shown schematically in Figure 15, and the corresponding material balance is given in Table 45. The material balance assumes an inlet temperature to the catalyst bed of 480°C and a maximum bed temperature of 650°C in order to prevent loss of catalyst surface area. Complete combustion of carbon monoxide, sulfur compounds and hydrocarbons is also assumed. Based on this material balance, a stack height of 41 m,[21] and no plume rise, the source severities for a 5.1 x 10^4 metric tons/yr plant would be 2.6 for SO_x, 0.47 for NO_x, and 1.0 for carbon black.

Catalytic incinerators have not been used previously in carbon black plants, and their applicability to these operations is uncertain. Some possible problem areas are:[21]

- Loss of incinerator efficiency as the catalyst ages.
- Catalyst poisoning by sulfur compounds.
- Formation of sulfur trioxide on the catalyst.
- Problems associated with periods of high carbon black loading due to leaks in bag filters.

Table 44. MATERIAL BALANCE FOR THERMAL INCINERATOR[21]

Stream:	Vent gas to incinerator	Air to incinerator	Incinerator stack gas
Temperature, °C:	232	27	870
Components	Flow rates,[a] kg/hr		
Hydrogen	563		
Carbon dioxide	3,518		15,627
Carbon monoxide	7,029		
Hydrogen sulfide	66		
Sulfur oxides	0.6		263
Methane	145		
Acetylene	174		
Carbon black	11		
Nitrogen	41,221	44,797	86,014
Oxygen	739	13,567	4,549
Water	36,465	635	42,560
Nitrogen oxides	8.2		15
Carbon disulfide	66		
Carbonyl sulfide	23		
TOTAL	90,029	58,999	149,028

[a] Blanks indicate no mass flow of component.

Table 45. MATERIAL BALANCE FOR CATALYTIC INCINERATOR[21]

Stream:	Vent gas to incinerator	Air to incinerator	Incinerator stack gas
Temperature, °C:	232	27	650
Component	Flow rates,[a] kg/hr		
Hydrogen	563		
Carbon dioxide	3,518		15,624
Carbon monoxide	7,029		
Hydrogen sulfide	66		
Sulfur oxides	0.6		263
Methane	145		
Acetylene	174		
Carbon black	11		4
Nitrogen	41,221	114,119	155,339
Oxygen	739	34,652	25,633
Water	36,465	2,033	43,959
Nitrogen oxides	8.2		11
Carbon disulfide	66		
Carbonyl sulfide	23		
TOTAL	90,029	150,804	240,833

[a] Blanks indicate no mass flow of component.

[b] A large amount of excess air is used to prevent the temperature in the catalyst bed from exceeding 650°C.

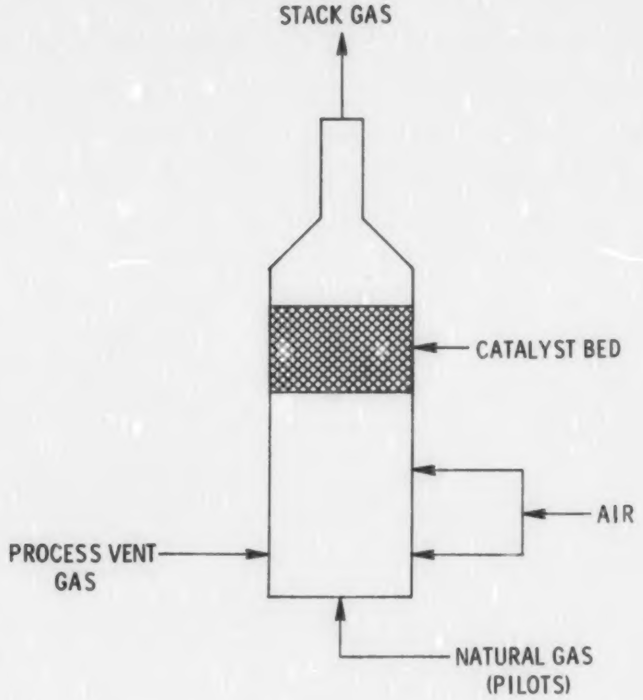

Figure 15. Catalytic incinerator for carbon black plant.[21]

2. Combustion Devices for New Plants

New carbon black plants can be designed to operate with steam-driven equipment. However, more steam can be produced by burning the process vent gas than can be utilized by the plant. If a market exists for exported steam, then a carbon monoxide boiler such as the one illustrated in Figure 14 might be the most economical combustion device. In the absence of a market for steam, the most economical device would probably be a flare or a thermal incinerator equipped with a waste heat boiler to supply the steam requirements of the plant. The latter unit is illustrated in Figure 16.

A material balance based on the process vent gas (stream 11) of Table 19 is given in Table 46. Complete combustion of all combustible species is assumed. Data from a similar unit in operation in a Canadian carbon black plant give combustion efficiencies of 99.6% for hydrogen sulfie and 99.8% for carbon monoxide.[46]

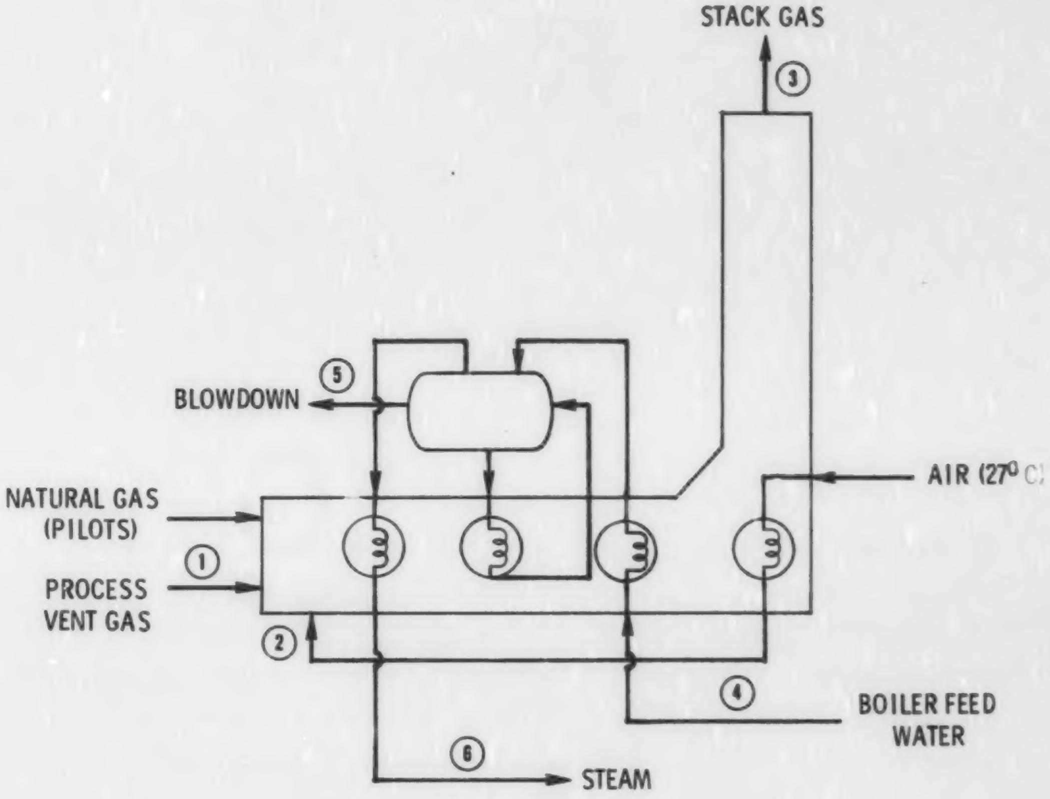
STACK GAS
③
⑤
BLOWDOWN
NATURAL GAS (PILOTS)
①
PROCESS VENT GAS
AIR (27° C)
②
④
BOILER FEED WATER
⑥
STEAM

Figure 16. Thermal incinerator with waste heat boiler.[21]

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[46] Source Testing of a Waste Heat Boiler. George D. Clayton Associates. EPA 75-CBK-3, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1975. 29 pp.

Table 46. MATERIAL BALANCE FOR THERMAL INCINERATOR WITH WASTE HEAT BOILER[21]

Stream no.:	1	2	3	4	5	6
Description:	Process vent gas	Preheated air	Stack gas	Boiler feed water	Boiler blowdown	Steam
Temperature, °C:	232	413	496	116	238	400
Gage pressure, kPa:[a]						3,103
Component	Flow rates,[b] kg/hr					
Hydrogen	563					
Carbon dioxide	3,518		15,627			
Carbon monoxide	7,029					
Hydrogen sulfide	66					
Sulfur oxides	0.6		263			
Methane	145					
Acetylene	174					
Carbon black	11					
Nitrogen	41,221	44,797	86,014			
Oxygen	739	13,567	4,549			
Water	36,465	635	42,560	25,973	1,246	24,727
Nitrogen oxides	8.2		15			
Carbon disulfide	66					
Carbonyl sulfide	23					
TOTALS	90,029	58,999	149,028	25,973	1,246	24,727

[a] Blanks indicate data not available.

[b] Blanks indicate no mass flow of component.

The process vent gas is burned with preheated air at 980°C. The only supplemental fuel required is natural gas for the incinerator pilots. Hence, this device is more efficient than the carbon monoxide boiler-thermal incinerator combination discussed in Section V.A.2. In addition to the Canadian plant mentioned above, at least one European plant employs a device of this type.[21]

Based on the material balance given in Table 46, a stack height of 41 m,[21] and no plume rise, the source severities for a 5.1×10^4 metric tons/yr plant would be 2.6 for sulfur oxides and 0.64 for nitrogen oxides.

3. Carbon Monoxide Recovery

A new process for the recovery of carbon monoxide from process gas streams has recently been described in the literature.[47] The process, termed Cosorb by its developer, Tenneco Chemicals, recovers carbon monoxide by absorption in a solvent consisting of copper(I) aluminum chloride ($CuAlCl_4$) in a toluene base. This process represents a possible alternative to combustion devices for control of carbon monoxide emissions.

A flow diagram for the Cosorb process is shown in Figure 17. The carbon monoxide containing feed gas first passes through a drying unit that removes water which would otherwise react with the copper(I) aluminum chloride. The feed gas is then contacted with the Cosorb solvent in a countercurrent absorber at ambient temperature and any practical pressure. The carbon monoxide is removed from the gas stream by formation of a chemical complex with the solvent. Removal efficiencies of up to 99% by volume are feasible.

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[47] Haase, D. J. New Solvent Cuts Costs of Carbon Monoxide Recovery. Chemical Engineering, 82:52-54, 1975.

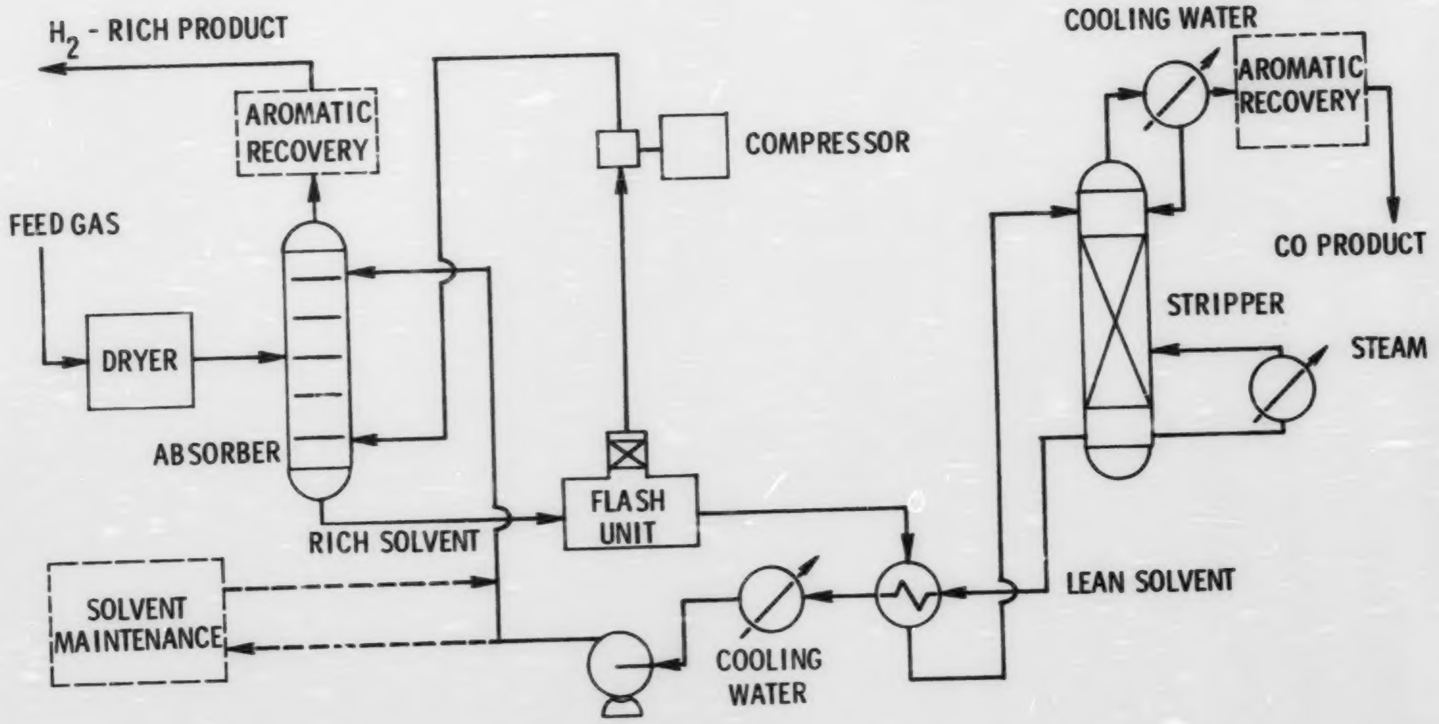
H$_2$ - RICH PRODUCT
AROMATIC RECOVERY
FEED GAS
DRYER
ABSORBER
RICH SOLVENT
SOLVENT MAINTENANCE
COMPRESSOR
FLASH UNIT
COOLING WATER
LEAN SOLVENT
COOLING WATER
AROMATIC RECOVERY
CO PRODUCT
STRIPPER
STEAM

Figure 17. Cosorb process for carbon monoxide recovery from industrial gases[47]

The carbon monoxide-rich solvent from the absorber is sent to a flash unit where those compounds which were physically (as opposed to chemically) absorbed in the toluene are separated from the solvent. The vapor stream from the flash unit is compressed and recycled to the absorber.

Carbon monoxide is recovered from the solvent in a stripping column. The stripping action of the toluene solvent base, together with heat supplied by low-pressure steam, results in an overhead stream which is typically greater than 99% carbon monoxide by volume. As shown on the flowsheet, toluene recovery systems may be required on both the carbon monoxide product stream and the absorber tail gas. These systems may employ compression, refrigeration, activated carbon, or non-volatile-liquid scrubbing.

Lean solvent from the stripping column is recycled to the absorber after heat exchange with the stripper feed. A solvent maintenance section may be needed to remove compounds other than carbon monoxide which are complexed by the solvent. For example, hydrogen sulfide and sulfur dioxide both react with the Cosorb solvent to some extent. Hence, the possibility exists for removing these compounds, as well as the carbon monoxide, from the process vent gas. The carbon monoxide recovered from the stripping column is of sufficient purity to be used for chemical synthesis.

4. Current Research Studies

Industry research projects in air pollution control are concerned with reducing the volume of vent gas which must be processed. The methods being studied include the following:[21]

- Operation of the reactors at pressures up to several atmospheres to reduce the gas volume and provide more efficient operation of combustion control equipment.

However, the operating pressure range is limited in practice since reactor pressure is one of the variables that determine the type and quality of black produced.

- Use of alternate heat exchange systems to minimize the amount of quench water required. A reduction in the amount of quench water would improve the heating value of the vent gas and reduce its volume.
- Substitution of oxygen for air in the reactor feed. Pilot plant tests have been unsuccessful because the use of pure oxygen results in a flame temperature which is too high for the furnace refractory. However, this modification merits further study since, in addition to reduced emissions, it could result in higher product yields and increased reactor capacity. In addition, the vent gas could be used as a synthesis gas for the Fischer-Tropsch process or for ammonia production, thus providing a valuable energy resource (see the following paragraph).
- Recycle of the vent gas to the reactor. This method of control has also been unsuccessful because the low heating value of the vent gas results in a flame temperature which is too low for high-quality blacks. If the water and nitrogen content of the vent gas could be reduced as indicated above, vent gas recycle might prove to be feasible. A process employing oxygen feed and vent gas recycle to produce carbon black and synthesis gas was patented in 1954.[17] However, no experimental results were presented to support the feasibility of the proposed process. A block flow diagram of the patented process is presented in Figure 18.
- Use of desulfurized feedstocks to reduce sulfur and trace metal emissions. One problem with this procedure is that hydrotreating reduces the aromatic content of the oil. This reduction results in lower carbon black yields and reduced reactor capacities.

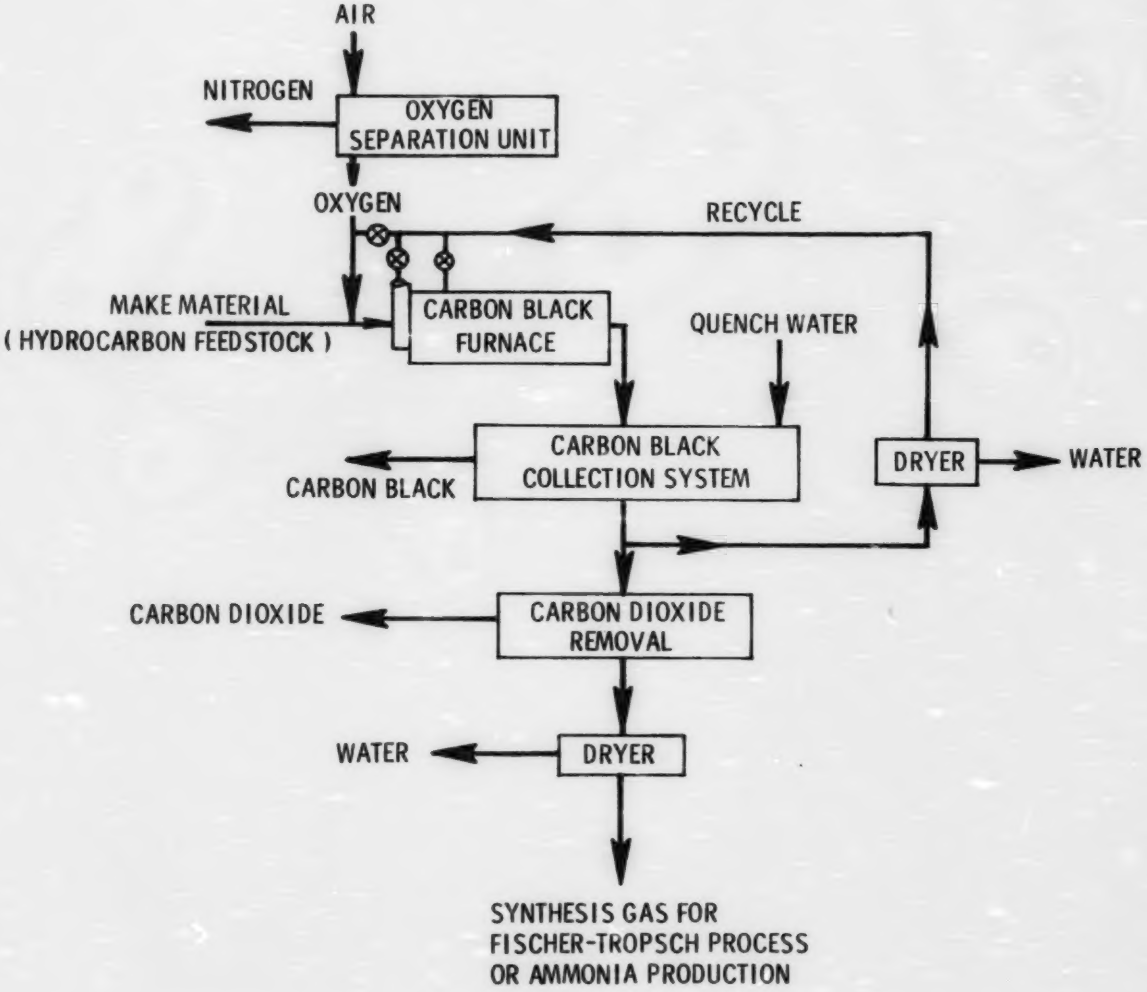
AIR
NITROGEN
OXYGEN SEPARATION UNIT
OXYGEN
RECYCLE
MAKE MATERIAL
(HYDROCARBON FEEDSTOCK)
CARBON BLACK FURNACE
QUENCH WATER
CARBON BLACK COLLECTION SYSTEM
CARBON BLACK
DRYER
WATER
CARBON DIOXIDE
CARBON DIOXIDE REMOVAL
WATER
DRYER
SYNTHESIS GAS FOR
FISCHER-TROPSCH PROCESS
OR AMMONIA PRODUCTION

Figure 18. Block diagram for production of carbon black and synthesis gas[17]

SECTION VI

GROWTH AND NATURE OF THE INDUSTRY

A. PRESENT TECHNOLOGY

Carbon black is presently produced in the United States by two major processes: the furnace process and the thermal process. The furnace process accounts for more than 90% of total production, while the thermal process accounts for about 10%.

The furnace process consists of three basic steps: feedstock cracking, product recovery, and product modification. The first step involves the partial oxidation and thermal decomposition of the hydrocarbon feedstock in a refractory-lined furnace to produce finely divided carbon particles. The reactor effluent is water quenched to terminate the cracking reaction and prepare the effluent for the product recovery step.

Prior to 1965, most plants recovered the carbon black from the reactor effluent stream by means of electrostatic precipitators and cyclones, with or without wet gas scrubbers. Nearly all furnace black plants now use bag filters, which result in reduced particulate emissions as well as improved product yield. The bag filters either have been added on to existing recovery devices or have replaced them entirely. The exhaust gas from the bag filter units is normally vented to the atmosphere, although a few plants employ combustion devices to reduce carbon monoxide, hydrogen sulfide, and hydrocarbon emissions.

Product modification involves forming the raw carbon black into pellets to increase its bulk density for ease of transportation and handling. Pelletizing is accomplished by working the carbon black with water which is subsequently removed in a drying operation. Emissions from the dryer exhaust are controlled with bag filters or water scrubbers.

Most (two-thirds) plants also employ a plantwide vacuum cleanup system to minimize emissions from carbon black spills. This system may also be used to control emissions from carbon black storage tanks and packaging operations.

B. EMERGING TECHNOLOGY

Since about 1950, the trend in the carbon black industry has been toward the oil furnace process, due to its greater efficiency and versatility. This trend is illustrated in Figures 19 and 20, which depict the history of carbon black production by process and by raw material. The rising cost and limited supplies of natural gas in the United States are expected to result in the continuation of this trend. The channel process is no longer operated domestically; the last U.S. plant ceased operations in 1976.[24]

Recent technological emphasis in the industry has been on obtaining a greater degree of control over product properties. This has resulted in the advent of many new, "improved" carbon blacks.[48] The present state of technology is such that blacks having virtually any combination of particle size and structure level can be produced to meet new or existing processing requirements in the consuming industries.

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[48] Hael, R. The Improved Blacks: What They Are and Where to Use Them. Rubber World, 172:42-44, 1975.

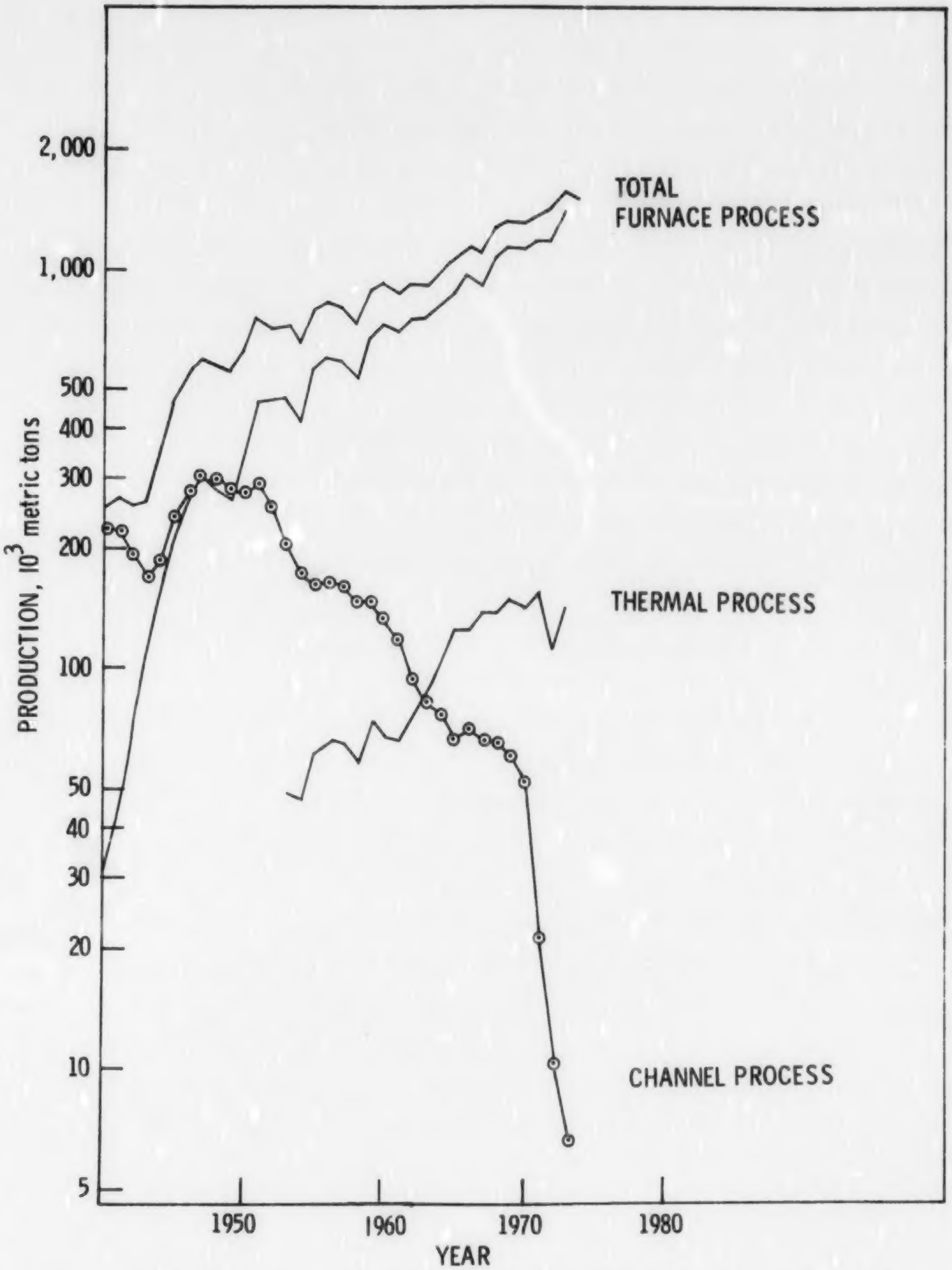

Figure 19. Carbon black production by process[1]

In the area of pollution control, the emphasis has been on the development and implementation of bag filters for product recovery, on dryer vents, pneumatic system vents, and, in some cases, on carbon black storage bin vents. Future developments will most likely center on combustion devices for controlling emissions of carbon monoxide, hydrogen sulfide, and hydrocarbons in the main process vent gas. Two plants presently flare the off-gas, and one plant employs a carbon monoxide boiler and thermal incinerator in combination. Although incineration provides effective emission control, most existing carbon black plants can neither use nor sell the steam which can be generated by incineration. Since the economics of this control method are unfavorable, new plants can be designed for steam-driven equipment.

C. MARKETING STRENGTHS AND WEAKNESSES

The consumption pattern of carbon black in the United States, presented in Table 47, shows that the rubber industry accounts for nearly 88% of total consumption and 93% of the carbon black consumed domestically. The ink, paint, and paper industries account for an additional 3% of the total, while exports and miscellaneous uses make up the remaining 9%. The recent consumption history of carbon black by the three major industrial users is depicted in Figure 21. The major categories are discussed in the following subsections.

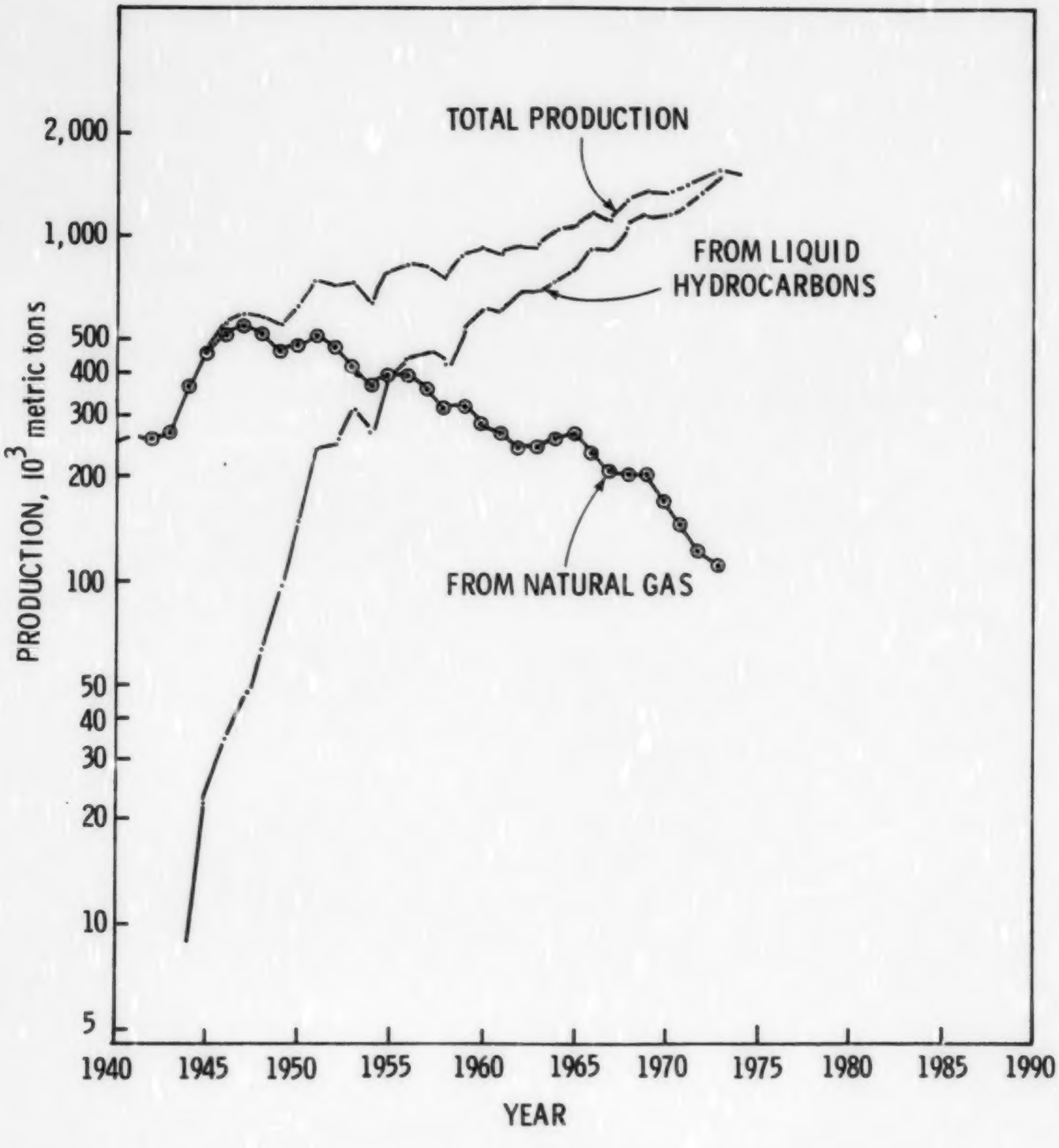

Figure 20. Carbon black production by raw material[1,26]

Table 47. 1974 CARBON BLACK CONSUMPTION[26]

Industry	Carbon black consumption, 10^3 metric tons	Percent of total sales
Rubber	1,326.8	87.6
Ink	37.7	2.5
Paint	8.6	0.6
Paper	1.6	0.1
Miscellaneous	52.6	3.5
Exports	87.5	5.7
TOTALS	1,514.8	100.0

1. Rubber Applications

It is estimated that 60% of the carbon black consumed by the rubber industry is used in tires of all types.[10] The remainder is used in a wide variety of other rubber products such as inner tubes, conveyor belts, wire and cable covering, motor mounts, fan belts, hose, gaskets, rubber heels, etc. The type and loading of carbon black vary with the application. For example, highly reinforcing blacks are required in tire tread, where resistance to abrasive wear is of major importance. In tire sidewalls and ply compounds, a minimum of hysteresis and low heat generation are required, and semi-reinforcing blacks are used. Carbon black constitutes an average of about 24% of the total weight of rubber in tires,[49] 30% to 40% of the total in wire and cable applications, and about 50% of the total in mechanical rubber goods

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[49] Richardson, H. M. Forecasting in the Rubber Industry. In: Hydrocarbons. The Dilemma in Forecasting. Presented at the joint meeting of the Chemical Marketing Research Association and the Commercial Development Association. New York, New York. May 1974. pp. 77-84.

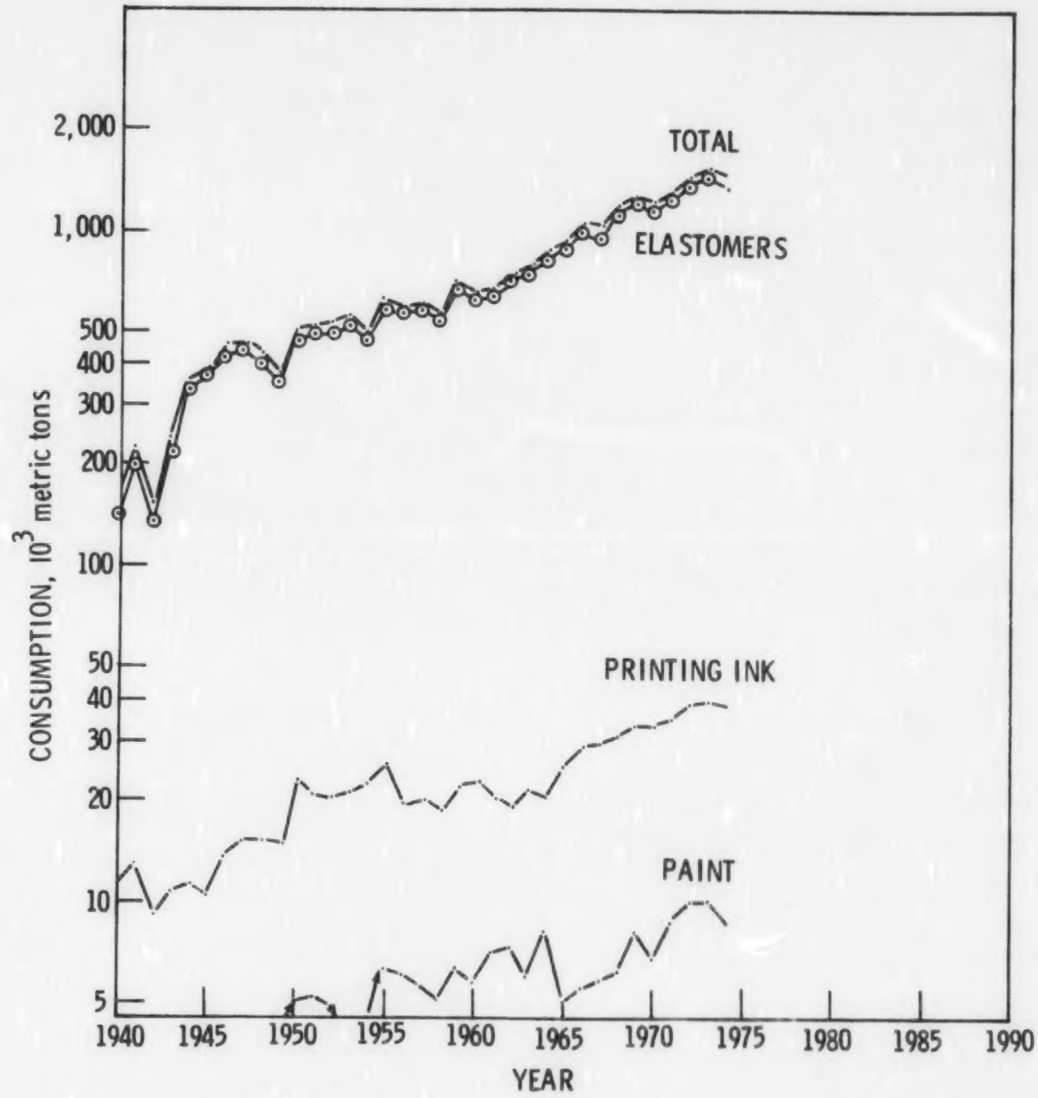

Figure 21. Domestic carbon black consumption history[1,26]

(belting, floor mats, molded products, etc.).[50] However, the loading varies widely depending on the product application. Usage of the various grades of carbon black in rubber products is summarized in Table 48.

From 1960 to 1973, total new rubber consumption in the United States increased at an average annual rate of 5.4%. In 1974, consumption decreased approximately 1% from the 1973 level.[51] Through 1980, consumption is expected to increase at a more moderate rate of from 2.4% to 3.8%,[49,52] primarily due to the effects of energy conservation programs and socio-economic trends on the transportation industry. This rate of growth will result in total new rubber consumption from 3.52 x 10^6 to 3.82 x 10^6 metric tons in 1980, compared to an estimated 3.05 x 10^6 metric tons in 1974. However, a growth rate of only 1.6% per year is forecast for rubber consumption for automotive tires.[49] This rate of growth will result in the use of 2.14 x 10^6 metric tons of rubber for tires in 1980, compared to 1.95 x 10^6 metric tons in 1974.

2. Printing Inks

Carbon black provides a pigment with extremely high opacity for use in printing inks. Since well over half of all inks are black, carbon black is the most widely used pigment in the industry. Loadings range from 15% to 22% in offset inks, 15% to 20% in most letterpress inks, 10% to 12% in letterpress news inks, and 8% to 12% in gravure inks (personal communication, C. B. Beck, Cabot Corporation, Pampa, Texas, 2/26/76).

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[50] Burgess, K. A., F. Lyon, and W. S. Stoy. Carbon. In: Encyclopedia of Polymer Science and Technology, Vol. 2. Wiley-Interscience Publications, New York, New York, 1965. pp. 820-836.

[51] Rubber Demand Faces Lower Growth Rate. Chemical and Engineering News, 52:12, 1974.

[52] Rubber Consumption to Increase. Rubber World, 172:83, 1975.

Table 48. APPLICATIONS OF CARBON BLACK IN THE RUBBER INDUSTRY[2]

Type	General properties in rubber	Typical uses
Oil furnace blacks		
Super abrasion	Maximum reinforcement; hard processing; high heat buildup	Tire treads and camelback; heels and soles of shoes; mechanical goods
Intermediate super abrasion	Fully reinforcing; good processing smoothout; medium heat buildup; good flex resistance	Tire treads and camelback; heels and soles of shoes; mechanical goods
Intermediate super abrasion - low structure	Good reinforcement; low heat buildup; low modulus; softer compounds	Tire treads and other abrasive service applications
Intermediate super abrasion - high structure	Excellent reinforcement; excellent processing and extrusion; high modulus	Tire treads and high abrasive service applications; difficult processing elastomers
High abrasion	Fully reinforcing; good processing smoothout; medium heat buildup; good flex resistance	Tire treads and camelback; heels and soles of shoes; mechanical goods
High abrasion - low structure	Channel black (EPC) properties; low heat buildup; low modulus	Channel black replacement in natural rubber and off-road tire treads
High abrasion - high structure	Fully reinforcing; superior processing and extrusion properties; high modulus	Tire treads and other high abrasive services, particularly in difficult processing elastomers
Fast extruding	Good reinforcement and resilience; good processing smoothout; low compression set	Tire carcass, tread base, and sidewall; butyl innertubes; hose; extruded stripping
General purpose	Moderate reinforcement; high resilience; low compression set; good processing smoothout	Tire carcass, tread base, and sidewall; sealing rings; cable jackets; hose; soling; extruded stripping
Conductive furnace	Excellent electrical conductivity; good retention after overmilling or flexing	Antistatic and conductive rubber goods; belts; hose; flooring

Table 48 (continued). APPLICATIONS OF CARBON BLACK IN THE RUBBER INDUSTRY[2]

Type	General properties in rubber	Typical uses
Gas furnace blacks[a]		
Fine furnace	Good reinforcement; moderate heat buildup	Truck tire carcass, breaker, and cushion
High modulus	Moderate reinforcement and resilience; easy processing	Tire carcass and sidewall; footwear; mechanical goods
Semireinforcing	Semireinforcing; high loading capacity; easy processing; good resilience and flex resistance	Tire carcass and bead insulation; mechanical goods; footwear and soling; wire jackets; belts; hose; packings
Thermal blacks		
Fine thermal	Low reinforcement; low hardness; high elongation; good tear resistance; high resilience; good flex resistance	Natural rubber innertubes; inflations; footwear uppers; mechanical goods
Medium thermal	Lowest reinforcement; high loading capacity; soft stocks; high resilience; low stress-strain properties	Wire insulation and jackets; mechanical goods; footwear; belts; hose; packings; stripping mats; proofed goods
Channel blacks[b]		
Medium processing	Fully reinforcing; medium in processing and in properties	Tire treads; heels and soles of shoes; mechanical goods
Easy processing	Fully reinforcing; easy processing; low hysteresis	Tire treads; heels and soles of shoes; mechanical goods

[a] Gas furnace blacks are no longer available. Similar blacks are now produced by the oil furnace process.

[b] Channel blacks are no longer produced domestically; however, they are still available on the international market. Similar blacks are now produced by the oil furnace process.

News inks, which account for more than 50% of production, contain carbon black dispersed in a petroleum oil. Although channel blacks were used in these inks for many years, they have been largely replaced by HAF grade oil furnace blacks. Furnace blacks in the particle size range from 25 nm to 75 nm are the most widely used in inks, often in combination with medium particle size channel blacks. Furnace blacks alone tend to develop a blue undertone, whereas channel blacks develop a browner undertone. Coarse furnace blacks are often used in carbon-paper inks, which contain mixtures of hard and soft waxes and mineral oils. Conductive inks used in printed circuitry are prepared with high concentrations of conductive carbon blacks. Applications of carbon blacks in the ink and related industries are summarized in Table 49.

The consumption of printing ink increased at an average annual rate of 4% from 1960-1974, as did the consumption of carbon black for printing inks.[1] While this rate of growth can be expected to continue through 1980, the effect on total carbon black consumption will be minor due to the small percentage of total consumption involved.

3. Paint and Coatings

The paint industry employs a wider range of carbon blacks (as pigments) than any other industry. The finest particle, high-color blacks (10 nm to 13 nm) are used in thermosetting acrylic finishes for automobiles and appliances. Medium-color channel and furnace blacks (14.5 nm to 25 nm) are used in general purpose maintenance and utility paints, while coarser blacks (25 nm to 40 nm) are used in drum enamels, chassis paints, and other inexpensive coatings. Carbon black usage in the paint industry is summarized in Table 49.

Table 49. APPLICATIONS OF CARBON BLACK IN THE INK, PAINT, PAPER, AND PLASTICS INDUSTRIES[2]

Type	Applications
Oil furnace blacks	
High abrasion	Newspaper and publication inks; black paper; carbon paper; conductive paints
Fast extruding	Blue tone and high color strength applications
General purpose	Tinting and shading paints and plastics
Conductive furnace	Conductive paints, plastics, and antistatic compounds
Gas furnace blacks[a]	
Fine furnace	Gravure and news inks; black paper; one-time carbons; paints; plastics
High modulus	Carbon paper inks; printing inks; maintenance paints; tinting dispersions
Semireinforcing	Blue tone and low oil absorption; printing and gravure inks; one-time carbon paper
Thermal blacks	
Fine thermal	Tinting in many applications
Medium thermal	Pigment in plastics and utility paints
Channel blacks[b]	
High color channel	Jettest carbon blacks; used in lacquers, enamels, and coloring plastics
Medium color channel	Enamels; plastics coloring and light stabilization
Regular color channel	Plastics; news and book inks; carbon paper; utility paints; black paper
Medium flow channel	Good flow properties in inks; used in paints, coloring nylon and other fibers
Long flow channel	Lithographic inks; letterpress ink; carbon paper; typewriter ribbon inks

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[a] Gas furnace blacks are no longer available. Similar blacks are now produced by the oil furnace process.

[b] Channel blacks are no longer produced domestically; however, they are still available on the international market. Similar blacks are now produced by the oil furnace process.

Carbon black consumption by the paint industry increased at an average annual rate of 4% from 1960 to 1973.[1] Consumption in 1974 declined about 15% from the 1973 level, reflecting the recession in the construction and automotive industries. The annual growth rate is expected to average between 4% and 5% over the period 1975 - 1980. Again, this will have little impact on the overall demand for carbon black due to the relatively small amount involved.

4. Other Applications

The paper industry employs carbon black in the production of a variety of black papers, including album paper, leatherboard, wrapping and bag papers, opaque backing paper for photographic film, highly conducting and electrosensitive paper, and black tape for wrapping high voltage transmission cables. Channel blacks were formerly used for these applications, but have now been largely replaced by furnace blacks of the appropriate jetness and wetting characteristics. Typical loadings are in the range of 2% to 8% by weight of pulp.[2]

Carbon black is used in plastics as a pigment and, in some instances, for filling and reinforcement. For example, crosslinked polyethylene compounds for cable coatings or pipe may contain up to 50% furnace or thermal black. Carbon black also functions as a stabilizer, preventing degradation of the polymer by ultraviolet radiation. In addition to absorbing ultraviolet radiation, it is effective in terminating the free radical chains produced in the photochemical reaction. Conductive carbon black is used to produce conductive plastics, which are of importance in the wire and cable industry for semiconductive outer sheathing and strand shielding in high voltage cable.

Carbon black is also used for insulation for high temperature operations, for the fabrication of carbon brushes and electrodes, and in the production of antistatic phonograph records, and as a source of elemental carbon for ore reduction and carburizing, a fuel and adsorbent in liquid oxygen explosives, a grinding agent in the cement industry, and a pigment in linoleum, leather coatings, polishes, plastic tile, and concrete.

Exports have declined from a peak of 246 x 10^3 metric tons in 1960 to 88 x 10^3 metric tons in 1974, but have remained nearly static since 1969 (89 x 10^3 metric tons).[1]

5. Industry Forecast

It is obvious from Figure 21 that the total demand for carbon black is determined by the demand in the rubber industry. As previously noted, new rubber consumption is expected to increase at an annual rate of 2.4% to 3.8% through 1980. However, consumption for tires, which account for an estimated 60% of the carbon black used in the rubber industry, is expected to increase at a yearly rate of only 1.6%. Based on these figures, a growth rate of 2% to 2.5% per year through 1980 can be anticipated for carbon black. This rate of growth will result in the production of 1.73 x 10^6 to 1.79 x 10^6 metric tons in 1980 compared to 1.54 x 10^6 metric tons in 1974. By comparison, the average growth rate for carbon black from 1964 through 1974 was 4.3%.[1]

The oil furnace process will continue to dominate the industry in the foreseeable future. With the decline of the channel process, the oil furnace process has become the only source of the fine-particle blacks required for tire tread and other high reinforcement applications. In addition, the rising cost and dwindling supply of natural gas will prevent any major expansion in the thermal process, although it is possible to operate the latter process on liquid feedstocks. The same factors may also force the substitution of liquid hydrocarbons for natural gas as fuel in the oil furnace process.

The recent production history of the five major grades of oil furnace blacks is shown in Figure 22. It can be seen that the HAF grade blacks predominate, presently accounting for 40% of all carbon black produced in the U.S., and for nearly one-half of all furnace black production.

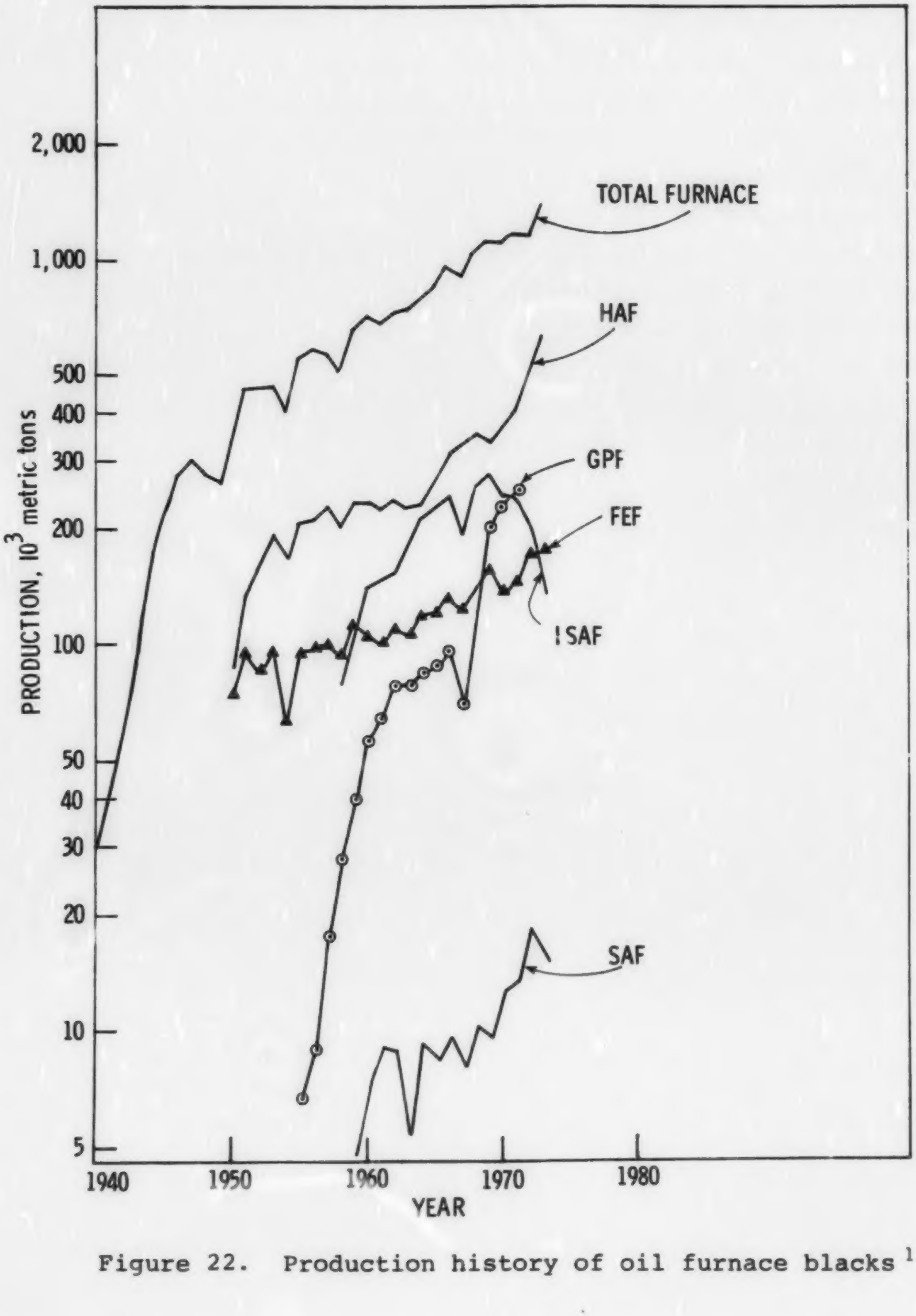

Figure 22. Production history of oil furnace blacks[1]

SECTION VII

APPENDIXES

A. Storage Tank Calculations

B. Description of Thermal Process

C. Plume Rise Calculations

D. ASTM Nomenclature for Carbon Black

E. Summary of Sampling and Analytical Methods

F. Results of Field Sampling Program

G. Simulated Source Severity Distributions

H. Remote Monitoring of Carbon Monoxide in Flare Off-Gas

APPENDIX A

STORAGE TANK CALCULATIONS

The procedure for calculating the emissions from storage tanks is outlined in this section. The equations given below were derived in references 28 through 32.

Step 1. Calculate the equivalent gasoline breathing loss:

$$L_y = \frac{24}{1000} {\frac{P}{14.7-P}}^{0.68} D^{1.73} H'^{0.51} (\Delta T)^{0.50} F_p C \qquad \text{(A-1)}$$

where L_y = equivalent gasoline breathing loss, bbl/yr

P = vapor pressure of material stored at bulk temperature, psia

D = tank diameter, ft

H' = average tank outage, ft

ΔT = average daily ambient temperature change, °F

F_p = paint factor

C = diameter factor

The calculations were performed for three different vapor pressures, 0.1, 0.2, and 0.4 psia. The tank diameter was calculated from the data in Table 14 by assuming a tank height of 50 ft. The average tank outage, i.e., freeboard, was taken as one-half the tank height, or 25 ft.

The average daily ambient temperature change, ΔT, was assumed to be 20°F, the national average value. The paint factor, F_p, was assumed equal to unity, the value for white paint in good condition. This factor can be as high as 14.6 for gray surfaces. The diameter factor, C, is equal to unity for tanks 30 ft or larger in diameter.

Step 2. Calculate the equivalent gasoline working loss:

$$F_g = \frac{3}{10,000} PVNK_T \qquad \text{(A-2)}$$

where F_g = equivalent gasoline working loss, bbl/yr
V = tank capacity, bbl
N = number of turnovers per year
K_T = turnover factor = 1.0 for $N \leq 36$
$= \frac{180 + N}{6N}$ for $N > 36$

Step 3. Compute total equivalent gasoline loss, L_g:

$$L_g = L_y + F_g \qquad \text{(A-3)}$$

Step 4. Compute petrochemical losses:

$$L = 0.08 \frac{M}{W} L_g \qquad \text{(A-4)}$$

where L = total petrochemical loss, bbl/yr
M = molecular weight of chemical stored
W = liquid density of chemical stored, lb/gal

Step 5. Calculate emission factor:

$$L_1 = L(42)(W) \qquad \text{(A-5)}$$

$$E' = \frac{L_1}{Cap} \qquad \text{(A-6)}$$

$$E = \frac{E'}{2} \qquad \text{(A-7)}$$

where L_1 = petrochemical loss, lb/yr
Cap = production capacity, ton/yr
E' = emission factor, lb/ton
E = emission factor, g/kg

The necessary input data for the above calculations are tabulated in Table A-1, while the results are summarized in Table A-2. The tank numbers in these tables correspond to those in Table 14.

Table A-1. STORAGE TANK INPUT DATA FOR CARBON BLACK PLANT

Tank number	1, 2, & 3
Input data	
Average ambient temperature change, °F	20
Material molecular weight	255
Liquid density, lb/gal	9.0
Vapor pressure,[a] psia	0.1;0.2;0.4
Tank diameter, ft	60
Tank outage, ft	25
Paint factor	1.0
Diameter factor	1.0
Turnover factor	1.0
Number turnovers per yr	6
Tank capacity, bbl	25,000

[a] Calculations were performed for each of the three vapor pressures shown; all other input data were unchanged for each vapor pressure level.

Table A-2. STORAGE TANK CALCULATION SUMMARY FOR CARBON BLACK PLANT

Tank no.	Vapor pressure, psia	Losses		Emission factor, g/kg
		gal/yr	lb/yr	
1,2,3	0.1	2,550	22,954	0.2416
1,2,3	0.2	4,273	38,453	0.4048
1,2,3	0.4	7,238	65,142	0.6857

APPENDIX B

DESCRIPTION OF THERMAL PROCESS

The thermal process for manufacture of carbon black is shown schematically in Figure B-1. Carbon black is produced by the thermal decomposition of natural gas in the absence of oxygen. The decomposition takes place in the reactor, which consists of two refractory-lined cylindrical furnaces, known as generators. The dimensions of the furnaces are 3.7 m (diameter) x 10.7 m (height). They are lined with an open checkerwork of silica brick.[2] The generators are heated to 1300°C by firing with a stoichiometric mixture of air and fuel. Natural gas is then admitted and decomposed to carbon and hydrogen as it passes through the hot checkerbrick.

Each generator is automatically alternated from the production cycle to the reheat cycle every five minutes, resulting in a continuous flow of product from the reaction area. The carbon black product is entrained in the effluent gas from the production cycle, which consists of 90% hydrogen, 6% methane, and 4% higher hydrocarbons.[2] After leaving the generator, the effluent gas passes through a cooling tower where its temperature is reduced to 125°C by water sprays.

The carbon black product is separated from the exhaust gas stream by means of cyclones and bag filters. The recovered black is then processed in the same manner as in the oil furnace process.

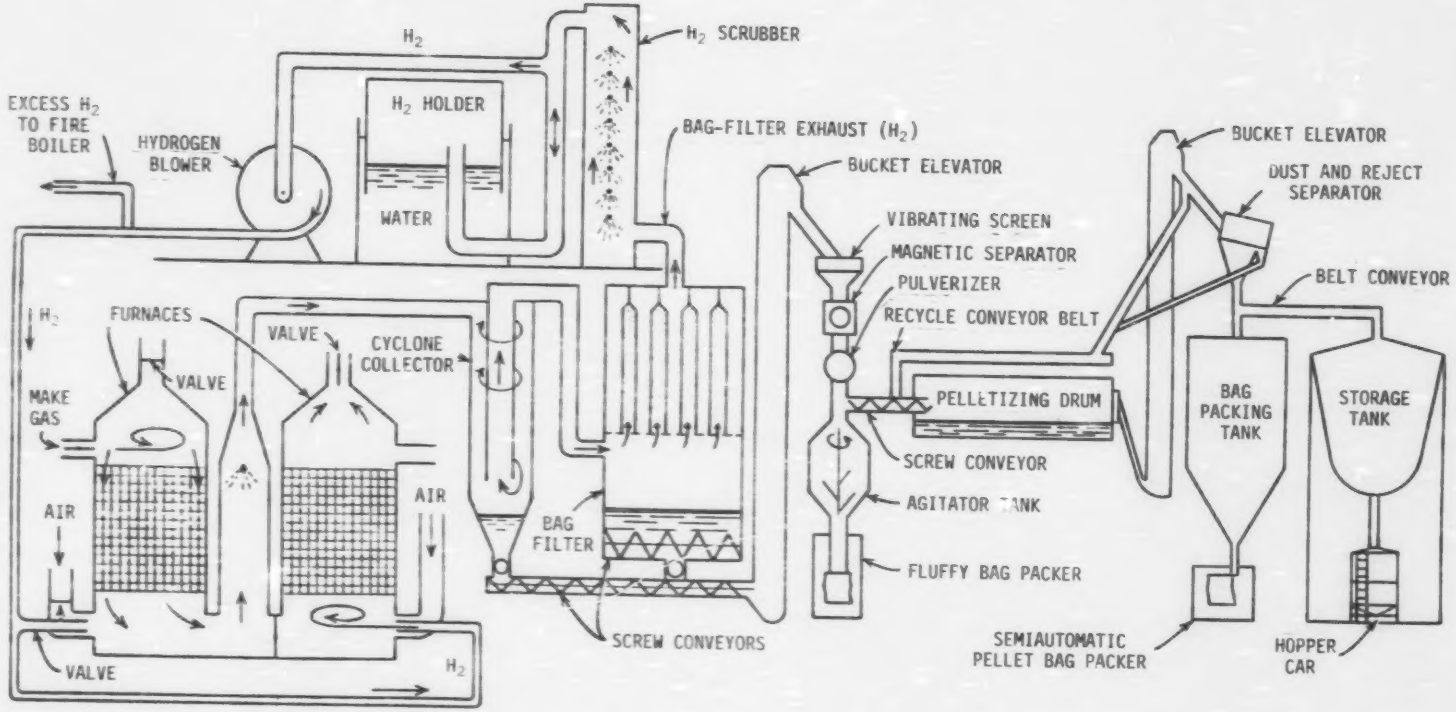
H_2
H_2 SCRUBBER
EXCESS H_2 TO FIRE BOILER
HYDROGEN BLOWER
H_2 HOLDER
WATER
BAG-FILTER EXHAUST (H_2)
BUCKET ELEVATOR
BUCKET ELEVATOR
DUST AND REJECT SEPARATOR
VIBRATING SCREEN
MAGNETIC SEPARATOR
PULVERIZER
BELT CONVEYOR
RECYCLE CONVEYOR BELT
H_2
FURNACES
VALVE
CYCLONE COLLECTOR
VALVE
MAKE GAS
PELLETIZING DRUM
BAG PACKING TANK
STORAGE TANK
SCREW CONVEYOR
AIR
AIR
AGITATOR TANK
BAG FILTER
FLUFFY BAG PACKER
SEMIAUTOMATIC PELLET BAG PACKER
HOPPER CAR
SCREW CONVEYORS
VALVE
H_2

Figure B-1. The thermal process for the manufacture of carbon black[2]

The hydrogen-rich vent gas from the bag filters is cooled, dehumidified, compressed, and used as fuel to reheat the generators. Since more hydrogen is produced than is required for reheating, the excess is used to generate steam and electricity to operate the plant.[2] Alternatively, the excess vent gas may be flared.

Atmospheric emissions from the thermal process consist of the following: (1) vent gas from the furnace which is on the reheat cycle; (2) boiler stack gas; (3) dryer vent gas; (4) pneumatic system (if used) vent gas; (5) vacuum cleanup system (if used) vent gas; and (6) fugitive emissions. The latter four emissions are similar to those from the oil furnace process since the operations which give rise to these emissions are similar in the two processes. Emissions (1) and (2) correspond to the main process vent gas in the oil furnace process. There is no emission point in the thermal process which corresponds to the oil storage tank vents in the oil furnace process.

The vent gas from the furnace reheat cycle consists primarily of combustion products of the fuel, which, as noted above, is 90% hydrogen. In addition, the vent gas contains carbon oxides formed by the combustion of carbon deposited on the checkerbrick during the production cycle. Approximately 50% of the carbon black formed in each cycle is deposited on the checkerbrick.[5]

The boiler stack gas consists of combustion products of the fuel gas (90% hydrogen) and natural gas that was used as supplementary fuel.

Comparison of emissions from the main process vent in the oil furnace process with the corresponding emissions (1) and (2) above from the thermal process shows the latter to be less severe. In particular:

- Emissions of hydrogen sulfide, carbon disulfide, carbonyl sulfide, and sulfur dioxide are much lower in the thermal process due to the very low sulfur content of the natural gas feedstock. (The hydrogen sulfide concentration in pipeline natural gas ranges from 0.2 ppm to 0.7 ppm, with an average value of 0.3 ppm.[53])
- Hydrogen and hydrocarbon emissions are much lower in the thermal process because the process off-gas is burned as fuel.
- Carbon monoxide emissions are lower in the thermal process because the decomposition of natural gas to form carbon black is carried out in the absence of oxygen. Any carbon monoxide formed by reaction of carbon black with water in the cooling tower is subsequently converted to carbon dioxide since the process off-gas is burned as fuel. Formation of carbon monoxide during the heating cycle is limited by the fuel composition, which is 90% hydrogen and 10% hydrocarbons. Thus, oxidation of carbon deposited on the checkbrick during the production cycle represents the main source of carbon monoxide emissions.
- POM and trace element emissions are lower in the thermal process because the feedstock is natural gas rather than aromatic fuel oil. Exceptions are emissions of trace elements which originate in the quench water; these emissions should be comparable in the two processes.

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[53] Finneran, J. A., L. J. Buividas, and N. Walen. Advanced Ammonia Technology. Hydrocarbon Processing, 51:127-130, April 1972.

- Nitrogen oxide emissions from the two processes should be comparable since the reactors are maintained at approximately the same temperature in both processes.

- Particulate emissions associated with the process off-gas are lowered for the thermal process since: (1) the same collection devices (cyclones, bag filters, scrubbers) are used in both processes; and (2) combustion of the thermal process off-gas further reduces the amount of carbon black emitted to the atmosphere. However, an additional emission of carbon black occurs in the thermal process when the furnaces are switched from the production to the reheating cycle. Loose carbon black deposited on the checkerbrick during the production cycle is emitted to the atmosphere in the form of a puff. There emissions occur at five minute intervals.[2,5,13]

APPENDIX C

PLUME RISE CALCULATIONS

The source severities presented in Section IV were calculated assuming no plume rise, i.e., the effective emission height was equated with the physical stack height. However, both the main process vent gas and the dryer vent gas have significant buoyancy and momentum, which result in plume rise. In this section, the effect of plume rise on the source severity is estimated.

Plume rise is estimated using Holland's equation:[54]

$$\Delta H = \frac{1}{\bar{u}} (1.5\ V_s D' + 0.04\ Q_H) \qquad \text{(C-1)}$$

where ΔH = plume rise, m

$\bar{u}$ = wind speed, m/s

V_s = stack gas exit velocity, m/s

D' = stack diameter, m

Q_H = heat emission rate, kcal/sec

The heat emission rate is calculated as follows:

$$Q_H = \frac{\pi D'^2}{4} V_s \frac{P'M'}{R} C_P \left(\frac{T_s - T_a}{T_s}\right) \qquad \text{(C-2)}$$

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[54] Briggs, G. A. Plume Rise. In: Critical Review Series. U.S. Atomic Energy Commission, Technical Information Center, Oak Ridge, Tennessee, 1969. 81 pp.

where P' = atmospheric pressure, dyne/m^2

R = gas constant = 8.314×10^5 dyne - m/g mole - °K

M' = molecular weight of stack gas, g/g mole

C_p = heat capacity at constant pressure of stack gas, kcal/g - °K

T_s = stack gas temperature, °K

T_a = ambient air temperature, °K

The values calculated from equation C-1 are generally too low. Based on extensive field data given in Reference 55, an average correction factor of 3 should be applied to the calculated plume rise. This value is in agreement with the correction factor of 2.92 recommended by Stümke.[54] Thus, the plume rise is estimated as three times the value computed from equation C-1.

1. MAIN PROCESS VENT

Based on data obtained at the sampling site in the present study and on the survey of operating plants given in Reference 21, the following values are used in the calculation for the main process vent:

$\bar{u}$ = 4.5 m/s (definition of source severity)

V_s = 21 m/s

D' = 0.9 m

P' = 1.01×10^{10} dyne/m^2

M' = 25

T_s = 492°K

T_a = 292°K

C_p = $3.4 \times 10^{-4} \dfrac{\text{kcal}}{\text{g-°K}}$

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[55] Moses, H. and M. R. Kraimer. Plume Rise Determination - A New Technique Without Equations. Journal of the Air Pollution Control Association, 22:621, 1972.

The value for C_p is the mean heat capacity between ambient temperature and T_s for a gas composed of water vapor, nitrogen, carbon dioxide, carbon monoxide, hydrogen sulfide, methane, acetylene, and oxygen in the proportions listed in Table 26 (Section IV.B). That is, only the major components of the stack gas were used to compute C_p.

Substituting the above values into equations C-1 and C-2 yields:

$$\begin{aligned}\Delta H &= \frac{1}{4.5}\ (28.67 + 0.04 \times 573) \\ &= \frac{1}{4.5}\ (28.67 \times 22.91) \\ &= 11.46 \text{ meters}\end{aligned}$$

Multiplying this value by 3 gives the corrected estimate of plume rise:

$$\Delta H_{\text{corrected}} = 34.4 \text{ meters}$$

Thus, if plume rise is taken into account, the source severities corresponding to the main process vent for the representative source (Tables 35, 36 and 37) should be corrected (i.e., multiplied) by the following factor:

$$\left(\frac{H_s}{H_s + \Delta H}\right)^2 = \left(\frac{25}{25 + 34.4}\right)^2 = 0.18 \cong 0.2$$

where H_s denotes the physical stack height.

2. DRYER VENT

Based on data obtained from the survey of operating plants given in Reference 21, the following values are used for the calculation of plume rise from the dryer vent:

$\bar{u}$ = 4.5 m/s (definition of source severity)

V_s = 6 m/s

D' = 0.6 m

P' = 1.01×10^{10} dyne/m^2

M' = 28

T_s = 642°K

T_a = 292°K

C_p = 2.8×10^{-4} kcal/g-°K

The values for M' and C_p correspond to a gas resulting from complete, stoichiometric combustion of methane in air.

Substituting the above values into equations C-1 and C-2 yields:

$$\Delta H = \frac{1}{4.5}\ (5.4 + 0.04 \times 88.0)$$

$$= \frac{1}{4.5}\ (5.4 + 3.5)$$

$$\Delta H = 2.0 \text{ m}$$

Multiplying this value by 3 gives the corrected estimate of plume rise:

$$\Delta H_{\text{corrected}} = 6.0 \text{ m}$$

Thus, if plume rise is taken into account, the source severities corresponding to the dryer vent for the representative source (Table 35) should be corrected (i.e., multiplied) by the following factor:

$$\left(\frac{H_s}{H_s + \Delta H}\right)^2 = \left(\frac{20}{20 + 6}\right)^2 = 0.59 \cong 0.6.$$

APPENDIX D

ASTM NOMENCLATURE FOR CARBON BLACK

The carbon black classification system adopted in 1967 by the American Society for Testing and Materials is presented in Tables D-1 and D-2. The first digit of the ASTM number designates the particle size of the black, as indicated in Table D-1. The next two numbers are arbitrarily assigned by an ASTM committee. However, this convention is not strictly adhered to, especially in the case of the newer blacks. For example, the particle size of grade N375 is approximately 23.5 nm,[48] so that it should be assigned to the 200 series.

Table D-2 is a partial listing of ASTM carbon black numbers together with the corresponding industry classifications.[56] The letters N and S denote normal rubber cure rate and slow rubber cure rate, respectively.

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[56] Standard Classification System for Carbon Blacks Used in Rubber Products. 1974 Annual Book of ASTM Standards. Part 38. American Society for Testing and Materials, Philadelphia, Pennsylvania, 1974. pp. 408-409.

Table D-1. ASTM CARBON BLACK PARTICLE SIZE CODE[56]

First Digit of ASTM number	Typical Particle Size, nm
0	1 to 10
1	11 to 19
2	20 to 25
3	26 to 30
4	31 to 39
5	40 to 48
6	49 to 60
7	61 to 100
8	101 to 200
9	201 to 500

Table D-2. ASTM CARBON BLACK NOMENCLATURE SYSTEM [a,b,56]

ASTM Number	Industry Classification	ASTM Number	Industry Classification
N110	SAF	N363	HAF-LS
N166	SAF-HS	N375	HAF
N195	SCF	N440	FF
S212	ISAF-LS-SC	N472	XCF
N219	ISAF-LS	N539	FEF-LS
N220	ISAF	N542	FEF-LS
N231	ISAF-LM	N550	FEF
N234	-[c]	N568	FEF-HS
N242	ISAF-HS	N601	HMF
N270	ISAF-HS	N650	GPF-HS
N285	ISAF-HS	N660	GPF
N293	CF	N683	APF
N294	SCF	N741	-[c]
S300	EPC	N754	SRF-LS
S301	MPC	N762	SRF-LM-NS
S315	HAF-LS-SC	N765	SRF-HS
N326	HAF-LS	N774	SRF-HM-NS
N327	HAF-LS	N785	MPF
N330	HAF	N787	SRF-I-HS
N332	HAF	N880	FT
N339	HAF	N881	FT
N347	HAF-HS	N907	MT-NS
N351	HAF-HS	N908	MT-NS
N356	-[c]	N990	MT
N358	SPF	N991	MT

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[a] Personal communication, C. B. Beck, Cabot Corporation, Pampa, Texas, 26 February 1976.

[b] Personal communication, H. J. Collyer, Cabot Corporation, Billerica, Massachusetts, 14 January 1976.

[c] No corresponding industry classification.

APPENDIX E

SAMPLING AND ANALYTICAL METHODS

1. SAMPLING METHODS

a. Location of Sampling Ports

The plant selected for sampling utilizes the processing scheme shown in Figure E-1 for handling the main process vent gas. Gases from the carbon black furnace and quencher enter the baghouse where carbon black product is recovered. The main process vent gas leaves the baghouse at 220°C (425°F) and 75 mm to 100 mm H_2O (3 in. to 4 in. H_2O) positive pressure in a 1.07 m (42 in.) circular duct. The main process vent gas is split into two streams--the flare stack gas and the fuel-user trunk line. The flare stack is 0.76 m (30 in.) in diameter. A backpressure control valve located at the base of the flare stack maintains a 75 mm to 100 mm H_2O (3 in. to 4 in. H_2O) positive pressure on the fuel-user trunk line which is also a 0.76 m (30 in.) duct that transfers ~50% of the main process vent gas through a splitter to a fuel-user manifold. Six 0.3 m (12 in.) ducts transfer the main process vent gas (fuel gas) to dryers used in the plant.

The main process vent gas was sampled at two locations shown in Figure E-1: (1) in the flare stack; and (2) in the feed duct to one of the fuel-users (dryers). At the first location, only velocity traverses were made in order to determine the portion of the vent gas being flared. The second location was sampled for particulate matter and trace elements; POM's, hydrocarbons, and organosulfur compounds; CO, CO_2, O_2, H_2S, COS, CS_2, and SO_2; H_2, N_2, H_2O, and NO_x.

The flare stack sampling ports are 35 mm (1.4 in.) in diameter (1 in. standard pipe) and are located 0.9 m (3 ft) above the backpressure valve and 2.7 m (9 ft) below the top of the flare stack. These ports are spaced 90° from each other. They are 1.2 pipe diameters downstream of the backpressure valve and 3.6 pipe diameters upstream of the tip of the flare. The fuel-user sampling ports are located 3 m (10 ft) downstream of the mainfold and 0.9 m (3 ft) upstream of the water seal.

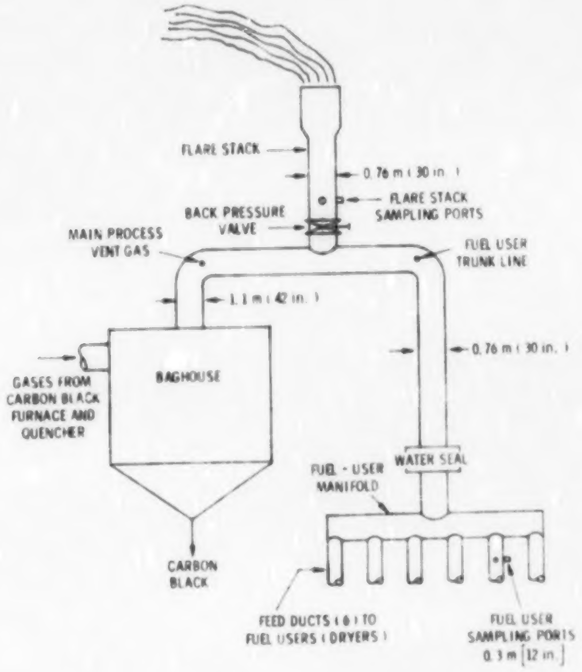
FLARE STACK
0.76 m (30 in.)
FLARE STACK SAMPLING PORTS
BACK PRESSURE VALVE
MAIN PROCESS VENT GAS
FUEL USER TRUNK LINE
1.1 m (42 in.)
0.76 m (30 in.)
GASES FROM CARBON BLACK FURNACE AND QUENCHER
BAGHOUSE
WATER SEAL
FUEL - USER MANIFOLD
CARBON BLACK
FEED DUCTS (6) TO FUEL USERS (DRYERS)
FUEL USER SAMPLING PORTS 0.3 m [12 in.]

Figure E-1. Process schematic showing disposition of main process vent gas and location of sampling ports

b. In-Stack Measurements

The methods used for sampling the various species in the main process vent gas are described in the following subsections.

(1) Particulate Matter and Trace Elements - A modification of the EPA Method 5 particulate sampling system was employed for these materials. The basic procedures and equipment used are specified in the Federal Register;[57] however, the sampling train was modified in order to collect both particulate and inorganic materials as specified in the Level I environmental assessment sampling procedure.[58]

The sampling system consisted of the Method 5 probe tip and probe assembly, with the probe containing a quartz liner. The probe was connected to a heated filter. For this study, the filter used was a Millipore Fluoropore® type FA filter, 60 mm in diameter with a nominal pore size of 1,000 nm. The exit side of the filter was connected to a series of four impingers designed to collect vaporous inorganic species. The first impinger contained 1×10^{-4} m^3 (100 ml) of 6M H_2O_2, while the second and third both contained 1×10^{-4} m^3 (100 ml) of 0.2M $(NH_4)_2S_2O_8$ and 0.02M $AgNO_3$. The fourth impinger contained 200 g of silica gel. The sampling system was operated as specified in the Federal Register by traversing and maintaining isokinetic conditions at each traverse point for sampling periods of 2 hours per run, for a total of three runs.

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[57] Environmental Protection Agency - Part II - Standards of Performance for New Stationary Sources - Proposed Amendments to Reference Methods. Method 5 - Determination of Particulate Emission from Stationary Sources. Federal Register, 41(111):23076-23083, 1976.

[58] Hamersma, J. W., S. G. Reynolds, and R. F. Maddalone. IERL-RTP Procedures Manual: Level I Environmental Assessment. EPA-600/2-76-160a, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1976. 131 pp.

Typical particle sizes for the reinforcing grade blacks (N330 and N351) produced during the sampling runs are 25 nm to 30 nm. Based on the work of Liu and Lee,[59] the collection efficiencies of Millipore Fluoropore® filters are greater than 99% for particles in this size range. In the work reported in Reference 59, monodispersed dioctyl phthalate (DOP) aerosols ranging in size from 30 nm to 1,000 nm were generated, and the efficiencies of filtration of Millipore Fluoropore® type FA filters with nominal 1,000 nm pores were measured as a function of particle size and pressure drop, the latter ranging from 10 mm Hg to 300 mm Hg. The results show that the efficiencies of the filters exceeded 99.99% over the entire operating range.

The material collected in the probe and filter was used to obtain the mass emission rate. After completion of the sampling run, the probe and probe tip were worked and brushed using high purity distilled water and a nylon brush. The liquid content of each impinger was measured, and the contents were then transferred to individual bottles. Each impinger was rinsed with three portions of distilled water, and this water was poured into a labelled bottle. The silica gel impinger contents were weighed and the material was placed in a bottle for shipment to the laboratory. Prior to shipment, all liquid containing samples were acidified with high purity concentrated nitric acid to a pH of 1 to 2 to prevent formation of precipitates and adsorption of trace elements on the glass bottle surfaces.

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[59] Liu, B. Y. H. and K. W. Lee. Efficiency of Membrane and Nucleopore Filters for Submicrometer Aerosols. Environmental Science and Technology, 10:345-350, 1976.

(2) Polycyclic Organic Materials, C-6 and Higher Hydrocarbons, and Organic Sulfur Compounds - The system employed for sampling these materials was a modification of the EPA Method 5 particulate sampling procedure.[57] For sampling, the standard fiberglass filter was replaced with a Millipore Fluoropore type FA filter and an organic trap 30 mm in diameter and 100 mm long. The organic trap contained XAD-2 resin and was placed between the filter and impingers. In addition, a gas cooler was employed between the filter and the resin trap in order to cool the gas and condense some of the water in the gas stream. This cooling is essential for carbon black sampling due to the 230°C (450°F) stack temperature and the high moisture content (45% to 50%) of the stack gas. The impinger system consisted of four impingers. The first impinger contained 1×10^{-4} m^3 (100 ml) of 10% KOH, the second and third impinger each contained 1×10^{-4} m^3 (100 ml) of toluene, and the fourth contained 200 g of 6-mesh to 16-mesh silica gel.

The sampling system was operated for three sampling runs by normal particulate sampling procedures, i.e., traversing and maintaining isokinetic conditions at each sampling point. At the completion of each run, the impinger contents were measured and transferred to amber bottles. The impingers were rinsed with the liquid they contained (10% KOH or toluene), and these rinsings were added to the proper bottle, which was then maintained at 0°C during shipment and holding for analysis. The filter was removed, placed in a petri dish, sealed, and held over ice at 0°C. The resin trap was sealed, placed in a plastic bag, and held over ice at 0°C. The entire train was rinsed with 1:1 methylene chloride-methanol, and these rinsings were stored in an amber bottle maintained at 0°C.

(3) Lower Molecular Weight Hydrocarbons - The hydrocarbon content of the gas stream was determined in two parts. Higher molecular weight compounds (above C_6) were collected by the XAD-2 trap employed in the POM collection system. Lower molecular weight compounds were analyzed on site by a portable gas chromatograph equipped with a flame ionization detector.

Samples for low molecular weight hydrocarbon analysis were obtained from the integrated gas samples collected during the Method 5 particulate-trace metal sampling runs and the POM sampling runs after portions of these integrated samples had been analyzed for gas composition as directed under Method 3, "Gas Analysis for Carbon Dioxide, Excess Air and Dry Molecular Weight," in the Federal Register.[60] The samples were collected over the entire particulate sampling period using Tedlar bags. Prior to use, the bags were evacuated and purged with nitrogen. A portion of the nitrogen was analyzed for hydrocarbons as a background check.

(4) H_2S, COS, CS_2, and SO_2 - Sampling for these materials was performed using EPA Method 15 as described in the Federal Register.[61]

(5) H_2, N_2, CO, CO_2, O_2, and H_2O - During the modified Method 5 particulate, trace element, and POM sampling,

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[60] Environmental Protection Agency - Part II - Standards of Performance for New Stationary Sources - Proposed Amendments to Reference Methods. Method 3 - Gas Analysis for Carbon Dioxide, Oxygen, Excess Air, and Dry Molecular Weight. Federal Register, 41(111):23069-23072,1976.

[61] Environmental Protection Agency - Standards of Performance for New Stationary Sources - Petroleum Refinery Sulfur Recovery Plants. Test Methods and Procedures. Federal Register, 41(193):43870-43874, 1976.

gaseous samples were collected using EPA Method 3, "Gas Analysis for Carbon Dioxide, Oxygen, Excess Air, and Dry Molecular Weight" integrated gas procedure.[60] The samples collected in the Tedlar bags were analyzed on site by the Orsat technique for CO, CO_2, O_2, and by difference for N_2 and H_2. For this type of industry, the Method 10 NDIR-CO procedure[62] is not appropriate since the concentration of CO may exceed the 5,000 ppm capability of the NDIR instrument. In addition to the Tedlar bag samples, grab samples were collected in evacuated glass sampling bulbs for later analysis of H_2 and N_2, and for confirming the CO, CO_2, and O_2 levels.

The moisture content of the gas stream was obtained from the Method 5 particulate-trace element sampling train impinger contents. As noted above, the increase in liquid level in the impinger was measured prior to rinsing the impinger with solvent and placing the liquid and rinses into a bottle.

(6) Nitrogen Oxides - Sampling for nitrogen oxides was performed using Method 7 as described in the Federal Register.[63,64]

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[62] Chapter 1 - Environmental Protection Agency - Part 60 - Standards of Performance for New Stationary Sources. Subchapter C - Air Programs. Subpart O - Standards of Performance for Sewage Treatment Plants. Federal Register, 39:9319-9321, 1974.

[63] Chapter 1 - Environmental Protection Agency - Part 60 - Standards of Performance for New Stationary Sources. Subchapter C - Air Programs. Method 7 - Determination of Nitrogen Oxide Emissions from Stationary Sources. Federal Register, 36:24891-24893, 1971.

[64] Environmental Protection Agency - Part II - Standards of Performance for New Stationary Sources - Proposed Amendments to Reference Methods. Method 7 - Determination of Nitrogen Oxide Emissions from Stationary Sources. Federal Register, 41(111):23085-23087, 1976.

c. Remote Monitoring

Remote monitoring of carbon monoxide in the flare off-gas is discussed in Appendix H.

d. Solid and Liquid Sampling

One sample of each of the two carbon black product types (N330 and N351) was collected for analysis of POM and trace element content.

One sample of liquid feedstock was obtained during run POM-1. The same shipment of feedstock was in use throughout the test period.

A sample of the quench feedwater was also obtained for trace element analysis. Prior to shipment to the laboratory, the sample was acidified with pure concentrated nitric acid to a pH between one and two.

2. ANALYTICAL METHODS

a. Particulate Matter and Trace Elements

The weight of particulate matter collected in the sampling train probe and filter was determined for each of the three trace metal runs as specified in EPA Method 5.[57] After the mass-loading determination, the particulate matter was prepared for trace element analyses. The particulate matter was ashed overnight in a Model 505 Low Temperature Asher manufactured by LTE Process Company of Waltham, Massachusetts. The ash was then digested in aqua regia and diluted to a known volume with distilled water. This volume was split into three fractions. One fraction was submitted to Accu-Labs Research, Inc., for spark source mass spectroscopy

(SSMS) analysis; a second fraction was diluted with distilled water to the proper acidity and salt concentration for analysis by the Jarrel Ash Atomcomp technique using inductively coupled argon plasma excitation (ICAP) at Monsanto Company's St. Louis Laboratory; the third fraction was analyzed for mercury, arsenic, and selenium by atomic absorption at MRC's Dayton Laboratory.

The material collected in the impingers was ashed, digested and submitted for trace element analysis as above. Thus, for each sampling run, characterization of the trace element contents was conducted on two separate samples, i.e., probe and filter combined, and the remainder of the sampling train after the filter.

b. Polycyclic Organic Materials and Other Organic Compounds

(1) Sample Pretreatment - The POM and hydrocarbon samples collected from the three POM runs were received from the field in the following forms:

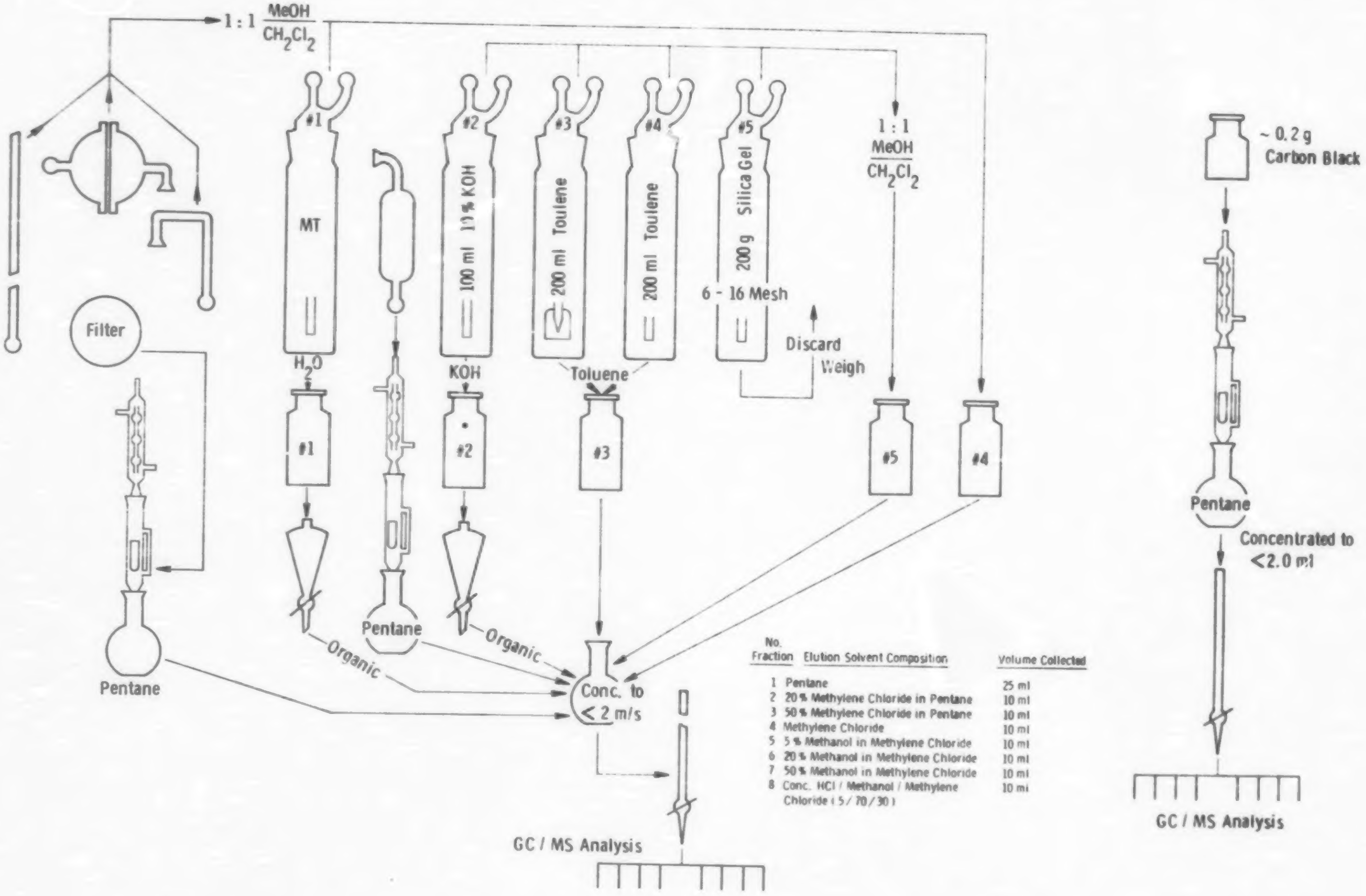
- Particulate samples from the probe washes
- Millipore Fluoropore type FA filter
- XAD-2 cartridge
- Contents of 10% KOH impinger including washings
- Contents of toluene impingers including washings

The XAD-2 trap was subjected to Soxhlet extraction with pentane for 24 hours. The pentane was then reduced to 5×10^{-6} m^3 ($\sim$5 ml) in volume by means of rotary evaporation. During rotary evaporation, a pressure >10 mm of N_2 and a water bath temperature of <45°C were maintained.

The 10% KOH impinger contents were extracted with methylene chloride, and the extract volume was reduced by rotary evaporation to about 5 ml. In a similar manner, the toluene impinger contents were reduced in volume to about 5 ml. Following the volume reduction, the above three samples were combined and separated into eight fractions on a silica gel column using the solvent systems shown in Figures E-2 and E-3 Each fraction was then reduced in volume with a Kuderna-Danish evaporator and transferred to a tare-weighed microweighing pan, and the remaining solvent was evaporated in air. Each dried fraction was weighed and then redissolved in a minimum quantity of methylene chloride.

All fractions were then examined employing a Digilab Model FTS-15B/D Fourier Transform Infrared (FTIR) Spectrometer to characterize the full range of organic constituents present, from the nonpolar aliphatic hydrocarbons to the polar sulfonic acids. This analysis was either qualitative or semiquantitative depending upon the complexity of the composition of each fraction.

Following infrared analysis, the second, third, and fourth fractions (containing the POM components) were diluted to 2×10^{-6} m^3 (2 ml) with methylene chloride and transferred to a Viton-septum sealed vial which was covered with aluminum foil and refrigerated until required for analysis. Just prior to analysis, the sample underwent one more volume reduction via the Kuderna-Danish method. The final volume was approximately 5×10^{-7} m^3 (500 μl). This volume size has been found to be optimum for detecting the POM peaks without obscuring contamination peaks.


1 : 1 MeOH / CH2Cl2
#1
MT
H2O
#1
Filter
Pentane
Pentane
Organic
#2
100 ml 10% KOH
KOH
#2
Organic
#3
200 ml Toulene
#4
200 ml Toulene
Toluene
#3
#5
200 g Silica Gel
6 - 16 Mesh
Discard
Weigh
1 : 1 MeOH / CH2Cl2
#5
#4
Conc. to < 2 m/s
GC / MS Analysis
~ 0.2 g Carbon Black
Pentane
Concentrated to <2.0 ml
GC / MS Analysis

No. Fraction	Elution Solvent Composition	Volume Collected
1	Pentane	25 ml
2	20 % Methylene Chloride in Pentane	10 ml
3	50 % Methylene Chloride in Pentane	10 ml
4	Methylene Chloride	10 ml
5	5 % Methanol in Methylene Chloride	10 ml
6	20 % Methanol in Methylene Chloride	10 ml
7	50 % Methanol in Methylene Chloride	10 ml
8	Conc. HCl / Methanol / Methylene Chloride (5 / 70 / 30)	10 ml

Figure E-2. Schematic of sample pretreatment for POM analysis

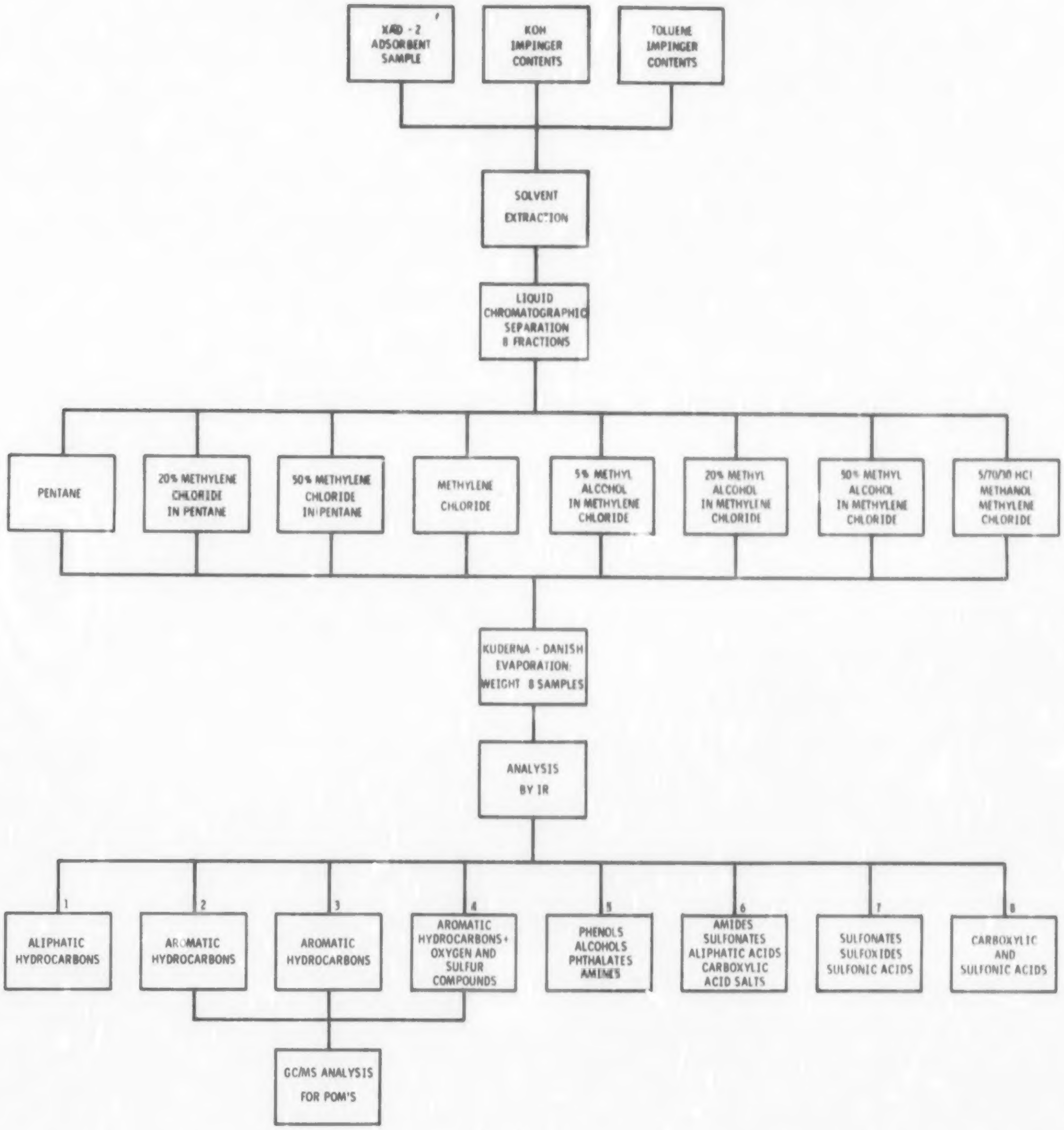

XAD - 2 ADSORBENT SAMPLE
KOH IMPINGER CONTENTS
TOLUENE IMPINGER CONTENTS
SOLVENT EXTRACTION
LIQUID CHROMATOGRAPHIC SEPARATION 8 FRACTIONS
PENTANE
20% METHYLENE CHLORIDE IN PENTANE
50% METHYLENE CHLORIDE IN PENTANE
METHYLENE CHLORIDE
5% METHYL ALCOHOL IN METHYLENE CHLORIDE
20% METHYL ALCOHOL IN METHYLENE CHLORIDE
50% METHYL ALCOHOL IN METHYLENE CHLORIDE
5/70/30 HCl METHANOL METHYLENE CHLORIDE
KUDERNA - DANISH EVAPORATION WEIGHT 8 SAMPLES
ANALYSIS BY IR
1
ALIPHATIC HYDROCARBONS
2
AROMATIC HYDROCARBONS
3
AROMATIC HYDROCARBONS
4
AROMATIC HYDROCARBONS + OXYGEN AND SULFUR COMPOUNDS
5
PHENOLS ALCOHOLS PHTHALATES AMINES
6
AMIDES SULFONATES ALIPHATIC ACIDS CARBOXYLIC ACID SALTS
7
SULFONATES SULFOXIDES SULFONIC ACIDS
8
CARBOXYLIC AND SULFONIC ACIDS
GC/MS ANALYSIS FOR POM'S

Figure E-3. Flow diagram for POM analysis[58]

An identical procedure was followed for pretreatment of the FA filter and the washings from the probe. Both particulate samples were extracted with pentane, combined, reduced in volume to $\sim 5 \times 10^{-6}$ m^3 ($\sim$5 ml), and subjected to liquid chromatographic separation on a silica gel column. After volume reduction via Kuderna-Danish evaporator and micro-weighing, Fourier Transform Infrared examination was conducted prior to specific POM analysis of the second, third, and fourth fractions. Thus, for each sampling run, characterization of the organic and POM contents was conducted on two separate samples, i.e., probe and filter combined, and the remainder of the train after the filter.

(2) Analytical Procedure for POM - In 1975, MRC developed its present analytical method for measuring POM content in environmental samples. The method employs the peak-area quantitation technique with computer reconstructed chromatograms from the (HP 5982-A) GC-MS. All data are collected in the electron impact (EI) mode because of the abundance of available EI-mass spectra. The chemical ionization (CI) mode of operation, which may provide greater sensitivity, is also available. MRC has found that GC-MS with a computer-controlled data system is the optimum of analytical accuracy, sensitivity, and speed.

The gas chromatographic separation is achieved using a 1.8-m (6-ft) Dexsil 400 glass column with temperature programming from 160°C for 2 min, rising to 280°C at 8°C/min, and becoming isothermal at 280°C. The carrier gas is helium at a flow rate of 0.5×10^{-9} m^3/s (30 μl/min).

The mass spectrometer, operating in the electron impact mode, is programmed to scan the 75-350 AMU range as the POM components elute from the gas chromatograph. The data system will reconstruct the chromatogram using the total ion mode. POM's are located by their molecular mass ions which are displayed using the selected ion mode (SIM). Their identity is confirmed by examining their mass spectra and retention times. Samples and standards are run in SIM for quantitation. SIM provides good stability, reproducibility, and sensitivity.

Calibration curves are prepared for each POM of interest using varying concentrations of the POM standards in methylene chloride, plotting mass ion peak area versus concentration, and determining response factors. POM peaks in samples are compared with standard curves that have been obtained under the same conditions: attenuation, injection volume [2×10^{-9} m^3 (2 μl)], and tuning condition. The tuning condition is important since it controls the relative sensitivity of the ions. Calibrations were made on the same day that the samples were analyzed. Our present (Jan. 1977) detection limit for POM's is $\sim$0.5 g/m^3 ($\sim$0.5 ng/μl) for a typical sample volume of 5×10^{-7} m^3 (500 μl). The following POM's are routinely analyzed at MRC:

Dibenzothiophene
Anthracene
Phenanthrene
Methylanthracenes }
Methylphenanthrenes } NR
9-Methylanthracene
Fluoranthene
Pyrene
Benzo[c]phenanthrene
Chrysene }
Benz[a]anthracene } NR

7,12-Dimethylbenz[a]anthracene
Benzo[b]fluoranthene
Benzo[a]pyrene (and isomers) - NR
3-Methylcholanthrene
Dibenz[a,b]anthracene
Indeno[1,2,3-cd]pyrene
Dibenzo[d,g]carbazole
Dibenzo[a,h]pyrene }
Dibenzo[a,i]pyrene } NR

NR = Not resolved.

Figure E-4 shows a typical chromatographic separation of the POM hydrocarbon standards. The top trace is a total ion (TI) reconstructed chromatogram of the standards. The traces below represent single ion chromatograms using the molecular mass ion of each individual POM. Each peak represents a specific POM hydrocarbon. The chromatogram for carbon black run POM-1 is shown in Figure E-5.

Table E-1 shows the results of reproducibility studies which have been conducted with POM standards at our laboratory. The standard deviations are listed for four replicate injections at the ∿0.2 g/m^3 (∿0.2 ng/μl) level for each POM sought. As noted, the variability becomes greater as the detection limits are approached. Table E-2 gives the results of a recovery study made at our laboratory using six POM's at the 100 g/m^3 (100 ng/μl) and 5 g/m^3 (5 ng/μl) concentration levels. Anthracene at high concentrations appears to present minor analysis problems.

(3) Organic Compound Analysis - The higher molecular weight hydrocarbons (above C_6) and organo-sulfur compounds collected by the sampling train were separated into eight fractions by the column chromatographic separation shown in Figure E-5. Each of the fractions was examined using the Digitab FTS-15B/D Fourier Transform Infrared Spectrometer (FTIR). The results of the FTIR analysis were used to determine whether the individual fractions should be examined by the GC/MS system to further identify the compounds present.

Organic compounds in the C_1 to C_6 molecular weight range were analyzed on site in the field, and no further laboratory analysis was done on these materials.

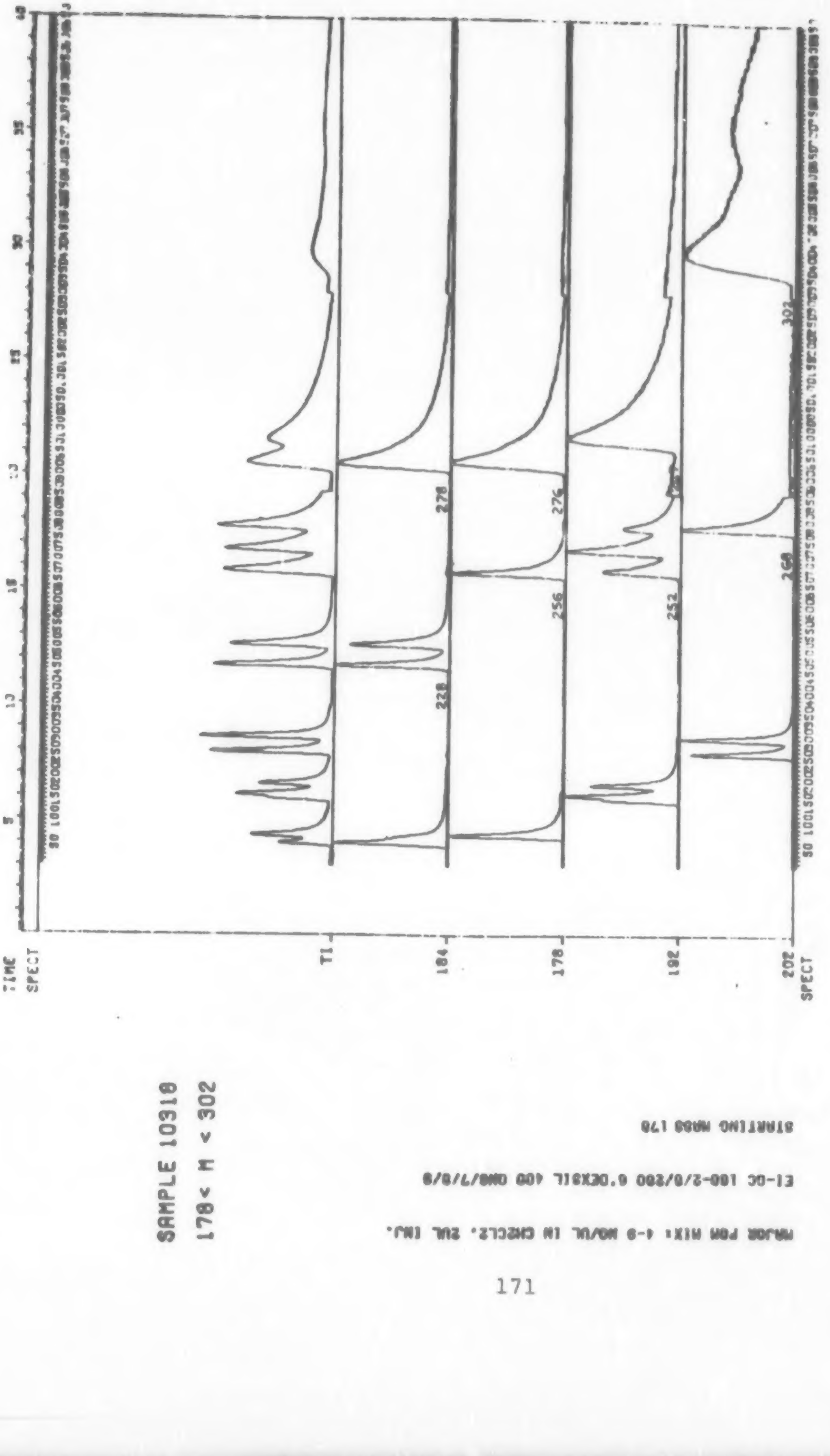


Figure E-4. Typical GC/MS chromatogram of POM hydrocarbon standards

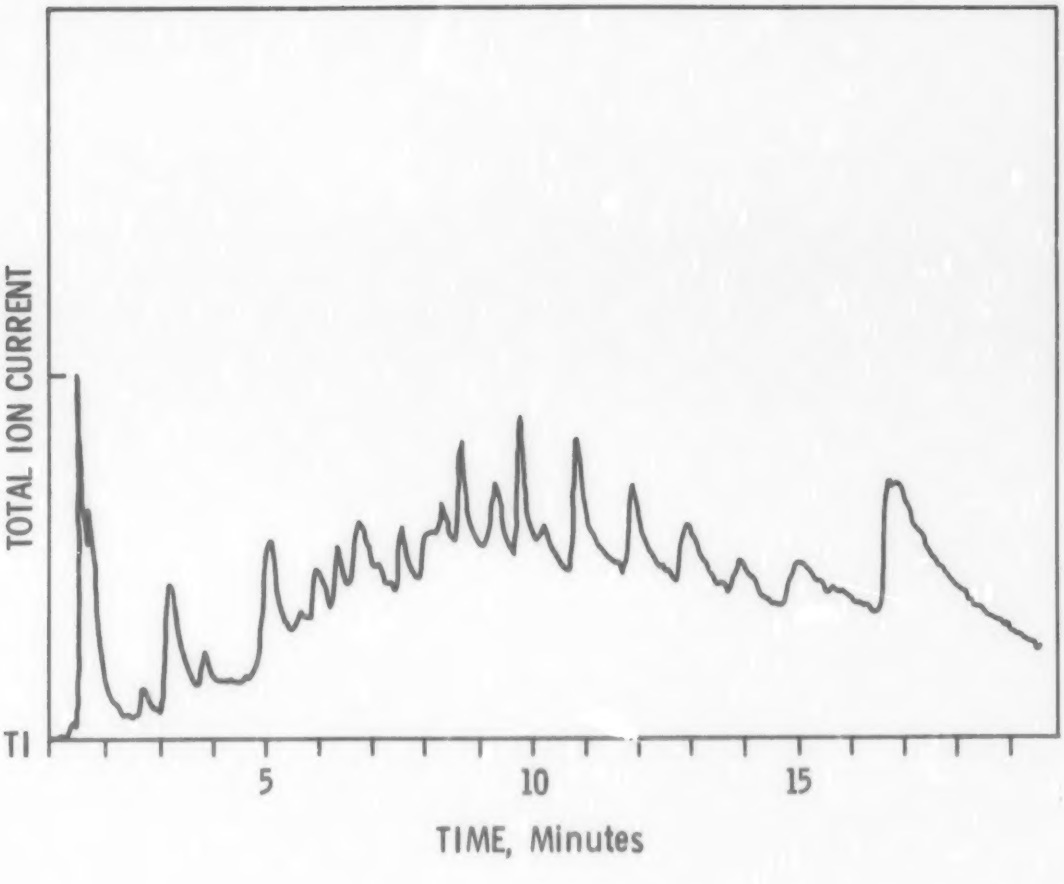


Figure E-5. Chromatogram for carbon black run POM-1

Table E-1. REPRODUCIBILITY STUDY USING POM STANDARDS

POM	% Standard deviation	
	$\sim$5 g/m^3 ($\sim$5 ng/μl) conc.	$\sim$2 g/m^3 ($\sim$2 ng/μl) conc.
Dibenzothiophene	3.4	11.8
Anthracene/Phenanthrene	3.7	11.5
Methylanthracenes/Methylphenanthrenes	5.9	11.9
9-Methylanthracene	7.7	10.1
Fluoranthene	5.8	5.4
Pyrene	5.3	9.0
Benzo[c]phenanthrene	3.0	9.1
Chrysene/Benz[a]anthracene	2.9	12.5
7,12-Dimethylbenz[a]anthracene	3.3	10.5
Benzo[b]fluoranthene	2.5	8.9
Benzo[a]pyrene	9.2	10.1
3-Methylcholanthrene	5.2	9.2
Dibenz[a,b]anthracene	1.7	6.4
Indeno[1,2,3-cd]pyrene	0.5	6.9
Dibenzo[c,g]carbazole	3.4	8.7
Dibenzo[a,h/a,i]pyrenes	3.2	7.8
Overall POM % Standard Deviation	4.2	9.4

Table E-2. PROCESSING RECOVERY STUDY USING POM'S

POM	% Recovered	
	$\sim$100 g/m^3 ($\sim$100 ng/μl) conc.	$\sim$5 g/m^3 ($\sim$5 ng/μl) conc.
Anthracene	80.1	93.9
Chrysene	95.5	98.0
7,12-Dimethylbenz[a]anthracene	94.4	98.3
Benzo[a]pyrene	94.9	98.3
3-Methylcholanthrene	95.8	96.1
Dibenz[a,b]anthracene	95.4	96.5

c. H_2S, COS, CS_2, and SO_2

These compounds were analyzed in the field using gas chromatographic separation and flame photometric detection as specified in EPA Method 15.[61]

d. H_2, N_2, CO_2, and O_2

The grab samples collected in the gas sampling flasks were analyzed for H_2, N_2, CO_2, and O_2 using mass spectroscopy.

e. Nitrogen Oxides

Nitrogen oxide emissions were analyzed following the procedure outlined in EPA Method 7.[63,64]

f. Analyses of Solid and Liquid Samples

Solid and liquid samples collected for analysis consisted of:

- Pelletized carbon black product (N330 and N351)
- Liquid carbon black feedstock
- Quench feedwater

Each of these samples was analyzed for trace elements. The two carbon black product samples were also analyzed for POM content.

The samples were prepared for trace element analysis as follows: five grams of each carbon black product and five grams of liquid feedstock were ashed in the LTE Low Temperature Asher described previously. The ash from each sample was digested in aqua regia and diluted to a known volume (250 ml) with distilled water. The quench water sample was boiled to remove any organic material and then diluted to the same volume (250 ml) with distilled water. Each of the samples was then split into three fractions. One fraction of each sample was sent to Accu-Labs, Inc., for analysis by SSMS. A second fraction of each sample was sent to Monsanto Company's St. Louis Laboratory for analysis by ICAP. The third fraction of each sample was analyzed for mercury, arsenic, and selenium by atomic absorption at the Dayton Laboratory.

The POM content of the carbon black samples was analyzed by the GC/MS approach as described in E.2.b. The sample preparation prior to analysis was similar to the technique used for particulate samples. The carbon black was ground and then extracted (Soxhlet) with pentane for 24 hours. The extracted material was separated into fractions as shown in Figure E-3. Fractions of 2 to 4 were reduced in volume as previously described, and analyzed for POM by the GC/MS method.

g. Carbon Monoxide in Flare Off-Gas

The measurement of carbon monoxide in the flare off-gas is discussed in Appendix H.

APPENDIX F

SAMPLING RESULTS

This appendix presents the results of a field sampling program conducted at a representative carbon black plant. Sampling was conducted on the main process vent gas. A total of six sampling runs was made, consisting of three trace element runs (1-TM, 3-TM and 4-TM) and three polycyclic organic material (POM) runs (POM-1, POM-2 and POM-3). Two blank runs (5-TM and POM-4) were also made to check the consistency of the sampling and analytical procedures. Run 2-TM was discarded during the test program due to a mechanical difficulty with the sampling apparatus which arose during testing. Samples of oil feedstock, quench water, and carbon black product were also analyzed.

Tables F-1, F-2 and F-3 present the emissions data for trace metal runs 1-TM, 3-TM and 4-TM, respectively. Tables F-4, F-5 and F-6 present the emissions data for polycyclic organic material runs POM-1, POM-2 and POM-3.

Tables F-7 and F-8 present a comparison of trace element runs with blank run 5-TM for the spark source mass spectroscopic (SSMS) and inductively coupled argon plasma (ICAP) analyses. For a number of elements, the concentrations in the blank sample were as great or greater than the concentrations in the run samples. For these elements, the emission factors listed in Tables F-1, F-2 and F-3 are not the actual emission factors, but represent upper bounds on the actual emission factors for these materials.

One possible source of anomalous values in the blank run is the glass containers used to store the samples. Silicon, sodium, calcium, magnesium, and aluminum are main constituents of glass. The reason for the high values of other elements, such as phosphorus, potassium, zinc, and iron is not known. These elements may have been present as impurities in reagents used in the sampling train or in those used to clean the glassware. They might also have been introduced during preparation of the samples for analysis.

A blank POM run (POM-4) was made and analyzed for POM content. No POM's were detected in the blank.

Table F-1. EMISSIONS DATA FROM RUN 1-TM

Emission	Concentration, mg/m^3		Emission factor, g/kg	
Inert gases				
Nitrogen	837,710		10,770	
Oxygen	15,700		200	
Carbon dioxide	70,185		900	
Water	477,150		6,135	
Criteria pollutants				
Particulate matter	7.4		0.09	
Sulfur oxides	-[a]		-[a]	
Nitrogen oxides	21		0.27	
Hydrocarbons	4,480		55	
Carbon monoxide	112,800		1,470	
Chemical substances				
Hydrogen	9,735		127	
Hydrogen sulfide	2,560		33	
Carbon disulfide	4,510		58	
Carbonyl sulfide	1,010		13	
Methane	2,450		32	
Acetylene	4,480		55	
Ethylene	-[a]		-[a]	
Propylene	-[a]		-[a]	
Propane	-[a]		-[a]	
Isobutane	-[a]		-[a]	
n-Butane	-[a]		-[a]	
Trace elements[b]				
Aluminum	0.17	{0.19}	2.1×10^{-3}	{2.4×10^{-3}}
Antimony	3.6×10^{-3}	{7.9×10^{-3}}	4.6×10^{-5}	{1.0×10^{-4}}
Arsenic	$<1.2 \times 10^{-3}$	{3.5×10^{-3}}	1.7×10^{-5}	{4.5×10^{-5}}
Barium	0.273	{8.1×10^{-2}}	3.5×10^{-3}	{1.0×10^{-3}}
Beryllium	$<1.8 \times 10^{-5}$		$<2.4 \times 10^{-6}$	
Bismuth	$<9.3 \times 10^{-4}$		$<1.2 \times 10^{-5}$	
Boron		{0.29}		{3.8×10^{-3}}
Bromine	7.5×10^{-4}		9.7×10^{-6}	

(continued)

Table F-1 (continued). EMISSIONS DATA FROM RUN 1-TM

Emission	Concentration, mg/m^3		Emission factor, g/kg	
Cadmium	1.5×10^{-3}	{4.0×10^{-3}}	2.0×10^{-5}	{5.2×10^{-5}}
Calcium	3.9	{5.0}	5.0×10^{-2}	{6.5×10^{-2}}
Cerium	1.8×10^{-4}		2.4×10^{-6}	
Cesium	$<9.2 \times 10^{-5}$		1.2×10^{-6}	
Chlorine	0.47		6.1×10^{-3}	
Chromium	5.4×10^{-2}	{1.2×10^{-2}}	7.0×10^{-4}	{1.6×10^{-4}}
Cobalt	1.9×10^{-2}	{3.7×10^{-3}}	2.4×10^{-5}	{5.0×10^{-5}}
Copper	1.8	{0.41}	2.4×10^{-2}	{5.3×10^{-3}}
Dysprosium	$<1.9 \times 10^{-4}$		$<2.4 \times 10^{-6}$	
Erbium	7.5×10^{-4}		9.7×10^{-6}	
Europium	$<2.8 \times 10^{-4}$		$<3.7 \times 10^{-6}$	
Fluorine	6.4×10^{-2}		8.3×10^{-4}	
Gadolinium	$<6.5 \times 10^{-4}$		$<8.6 \times 10^{-6}$	
Gallium	$<9.4 \times 10^{-5}$		$<1.2 \times 10^{-6}$	
Germanium	$<1.9 \times 10^{-4}$		$<2.4 \times 10^{-6}$	
Gold	$<1.9 \times 10^{-4}$		$<2.4 \times 10^{-6}$	
Hafnium	$<1.2 \times 10^{-3}$		$<1.6 \times 10^{-5}$	
Holmium	$<1.9 \times 10^{-4}$		$<2.4 \times 10^{-6}$	
Iodine	$<2.8 \times 10^{-4}$		$<3.7 \times 10^{-6}$	
Iridium	$<2.8 \times 10^{-4}$		$<3.7 \times 10^{-6}$	
Iron	0.47	{0.31}	6.1×10^{-3}	{4.0×10^{-3}}
Lanthanum	2.8×10^{-4}		3.7×10^{-6}	
Lead	5.7×10^{-2}	{5.4×10^{-2}}	7.4×10^{-4}	{7.0×10^{-4}}
Lithium	2.1×10^{-3}		2.8×10^{-5}	
Lutecium	$<1.9 \times 10^{-4}$		$<2.4 \times 10^{-6}$	
Magnesium	2.5	{0.14}	3.3×10^{-2}	{1.8×10^{-3}}
Manganese	1.7×10^{-2}	{4.5×10^{-3}}	2.2×10^{-4}	{5.8×10^{-6}}
Mercury		{1.4×10^{-4}}		{1.8×10^{-6}}
Molybdenum	7.7×10^{-3}	{7.7×10^{-3}}	1.0×10^{-3}	{1.0×10^{-4}}
Neodymium	$<3.7 \times 10^{-4}$		$<4.8 \times 10^{-6}$	
Nickel	0.13	{4.4×10^{-2}}	1.6×10^{-3}	{5.7×10^{-4}}
Niobium	$<2.8 \times 10^{-4}$		$<3.7 \times 10^{-6}$	
Osmium	$<3.7 \times 10^{-4}$		$<4.9 \times 10^{-6}$	
Palladium	$<2.8 \times 10^{-4}$		$<3.7 \times 10^{-6}$	
Phosphorus	1.3	{0.13}	1.7×10^{-2}	{1.7×10^{-3}}

(continued)

Table F-1 (continued). EMISSIONS DATA FROM RUN 1-TM

Emission	Concentration, mg/m^3		Emission factor, g/kg	
Platinum	<4.7×10^{-4}		<5.6×10^{-6}	
Potassium	3.6		4.6×10^{-2}	
Praseodymium	<2.8×10^{-4}		<3.7×10^{-6}	
Rhodium	9.4×10^{-5}		1.2×10^{-6}	
Rubidium	8.4×10^{-4}		1.1×10^{-5}	
Samarium	<1.3×10^{-3}		<1.7×10^{-5}	
Scandium	<2.8×10^{-4}		<3.7×10^{-6}	
Selenium	<1.8×10^{-4}	{9.4×10^{-5}}	<2.4×10^{-6}	{1.2×10^{-6}}
Silicon	0.77	{0.34}	1.0×10^{-2}	{4.4×10^{-3}}
Sodium	2.7	{1.4}	3.5×10^{-2}	{1.8×10^{-2}}
Strontium	7.2×10^{-3}	{5.7×10^{-3}}	9.4×10^{-5}	{7.3×10^{-5}}
Tantalum	<6.5×10^{-4}		<8.6×10^{-6}	
Terbium	<9.4×10^{-5}		<1.2×10^{-6}	
Tellurium	<1.9×10^{-4}		<2.4×10^{-6}	
Thallium	<3.7×10^{-4}		<4.8×10^{-6}	
Thorium	9.4×10^{-4}		1.2×10^{-5}	
Thullium	<2.8×10^{-4}		<3.7×10^{-6}	
Tin	8.1×10^{-2}	{4.6×10^{-2}}	1.0×10^{-3}	{5.9×10^{-4}}
Titanium	6.5×10^{-3}	{4.2×10^{-3}}	8.5×10^{-5}	{5.4×10^{-5}}
Tungsten	1.7×10^{-3}		2.2×10^{-5}	
Uranium	<5.6×10^{-4}		<7.3×10^{-6}	
Vanadium	1.6×10^{-3}	{5.1×10^{-3}}	2.1×10^{-5}	{6.6×10^{-5}}
Ytterbium	8.4×10^{-4}		1.1×10^{-5}	
Yttrium	7.5×10^{-4}		9.7×10^{-6}	
Zinc	5.9	{0.81}	7.7×10^{-2}	{1.0×10^{-2}}
Zirconium	6.2×10^{-3}		8.1×10^{-5}	
TOTAL Trace Elements[c]	22.6	{14.2}	0.3	{0.16}

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[a] Not detected at 1 ppm.

[b] Values in braces ({}) were determined by ICAP with the exception of those for arsenic, mercury, and selenium, which were determined by atomic absorption. Values not in braces were determined by SSMS.

[c] Totals do not include numbers recorded as upper bounds.

Table F-2. EMISSIONS DATA FROM RUN 3-TM

Emission	Concentration, mg/m^3		Emission factor, g/kg	
Inert gases				
Nitrogen	808,500		7,283	
Oxygen	19,630		175	
Carbon dioxide	71,980		650	
Water	473,760		4,270	
Criteria pollutants				
Particulate matter	15.2		0.14	
Sulfur oxides	–[a]		–[a]	
Nitrogen oxides	29.9		0.27	
Hydrocarbons	3,840		37	
Carbon monoxide	140,860		1,270	
Chemical substances				
Hydrogen	9,490		85	
Hydrogen sulfide	1,220		11.2	
Carbon disulfide	1,775		16	
Carbonyl sulfide	600		5.05	
Methane	2,025		20	
Acetylene	3,655		35	
Ethylene	138		1.2	
Propylene	–[a]		–[a]	
Propane	22		0.20	
Isobutane	10		0.09	
n-Butane	26		0.24	
Trace elements[b]				
Aluminum	0.28	(0.38)	2.5×10^{-3}	(3.4×10^{-3})
Antimony	1.6×10^{-3}	(2.6×10^{-2})	1.4×10^{-5}	(2.3×10^{-4})
Arsenic	$<1.3 \times 10^{-2}$	(4.7×10^{-3})	$<1.2 \times 10^{-4}$	(4.3×10^{-5})
Barium	0.35	(0.14)	3.1×10^{-3}	(1.2×10^{-3})
Beryllium	$<2.3 \times 10^{-4}$		$<2.1 \times 10^{-6}$	
Bismuth	$<4.6 \times 10^{-4}$		$<4.1 \times 10^{-5}$	
Boron		(0.68)		(6.1×10^{-3})
Bromine	6.8×10^{-4}		6.2×10^{-6}	

(continued)

Table F-2 (continued). EMISSIONS DATA FROM RUN 3-TM

Emission	Concentration, mg/m^3		Emission factor, g/kg	
Cadmium	1.4 x 10^{-3}	{6.9 x 10^{-3}}	1.2 x 10^{-5}	{6.2 x 10^{-5}}
Calcium	5.1	{9.8}	4.6 x 10^{-2}	{8.9 x 10^{-2}}
Cerium	4.6 x 10^{-4}		4.1 x 10^{-6}	
Cesium	<2.3 x 10^{-4}		<2.1 x 10^{-6}	
Chlorine	1.9 x 10^{-2}		1.8 x 10^{-4}	
Chromium	3.3 x 10^{-2}	{1.4 x 10^{-2}}	3.0 x 10^{-4}	{1.2 x 10^{-4}}
Cobalt	1.8 x 10^{-2}	{1.1 x 10^{-2}}	1.7 x 10^{-4}	{1.0 x 10^{-4}}
Copper	0.3	{0.1}	2.7 x 10^{-3}	{9.5 x 10^{-4}}
Dysprosium	<2.3 x 10^{-4}		<2.1 x 10^{-6}	
Erbium	1.1 x 10^{-3}		1.0 x 10^{-5}	
Europium	<4.6 x 10^{-4}		4.1 x 10^{-6}	
Fluorine	0.27		2.4 x 10^{-3}	
Gadolinium	3.0 x 10^{-3}		2.7 x 10^{-4}	
Gallium	<2.3 x 10^{-4}		<2.1 x 10^{-6}	
Germanium	<2.3 x 10^{-4}		<2.1 x 10^{-6}	
Gold	<2.3 x 10^{-4}		<2.1 x 10^{-6}	
Hafnium	<1.6 x 10^{-4}		<1.4 x 10^{-5}	
Holmium	<2.3 x 10^{-4}		<2.1 x 10^{-6}	
Iodine	<2.3 x 10^{-4}		<2.1 x 10^{-6}	
Iridium	<4.6 x 10^{-4}		<4.1 x 10^{-6}	
Iron	0.61	{0.33}	5.5 x 10^{-3}	{3.0 x 10^{-3}}
Lanthanum	2.3 x 10^{-4}		2.1 x 10^{-6}	
Lead	0.17	{9.4 x 10^{-2}}	1.6 x 10^{-3}	{8.5 x 10^{-4}}
Lithium	6.8 x 10^{-4}		6.2 x 10^{-6}	
Lutecium	<2.3 x 10^{-4}		<2.1 x 10^{-6}	
Magnesium	1.0	{0.54}	9.4 x 10^{-3}	{4.9 x 10^{-3}}
Manganese	7.8 x 10^{-3}	{7.1 x 10^{-3}}	7.0 x 10^{-5}	{6.4 x 10^{-5}}
Mercury		{4.7 x 10^{-2}}		{4.2 x 10^{-4}}
Molybdenum	2.2 x 10^{-2}	{1.6 x 10^{-2}}	2.0 x 10^{-4}	{1.4 x 10^{-4}}
Neodymium	<4.6 x 10^{-4}		<4.1 x 10^{-6}	
Nickel	0.16	{0.17}	1.5 x 10^{-3}	{1.5 x 10^{-3}}
Niobium	<2.3 x 10^{-4}		<2.1 x 10^{-6}	
Osmium	<6.9 x 10^{-4}		<6.2 x 10^{-6}	
Palladium	<4.6 x 10^{-4}		<4.1 x 10^{-6}	
Phosphorus	6.7 x 10^{-2}	{0.16}	6.1 x 10^{-4}	{1.4 x 10^{-3}}

(continued)

Table F-2 (continued). EMISSIONS DATA FROM RUN 3-TM

Emission	Concentration, mg/m^3		Emission factor, g/kg	
Platinum	$<6.9 \times 10^{-4}$		6.2×10^{-6}	
Potassium	1.4		1.3×10^{-2}	
Praseodymium	$<2.3 \times 10^{-4}$		$<2.1 \times 10^{-6}$	
Rhodium	$<2.3 \times 10^{-4}$		$<2.1 \times 10^{-6}$	
Rubidium	1.1×10^{-3}		1.0×10^{-5}	
Samarium	$<2.3 \times 10^{-4}$		$<2.1 \times 10^{-6}$	
Scandium	$<4.6 \times 10^{-4}$		$<4.1 \times 10^{-6}$	
Selenium	$<2.3 \times 10^{-4}$	$\{2.3 \times 10^{-4}\}$	$<2.1 \times 10^{-6}$	$\{2.0 \times 10^{-6}\}$
Silicon	1.4	{0.68}	1.3×10^{-2}	$\{6.2 \times 10^{-3}\}$
Sodium	4.4	{2.4}	3.9×10^{-2}	$\{2.1 \times 10^{-2}\}$
Strontium	9.8×10^{-3}	$\{9.6 \times 10^{-3}\}$	8.9×10^{-5}	$\{8.7 \times 10^{-5}\}$
Tantalum	$<2.3 \times 10^{-4}$		$<2.1 \times 10^{-6}$	
Terbium	$<2.3 \times 10^{-4}$		$<2.1 \times 10^{-6}$	
Tellurium	$<2.3 \times 10^{-4}$		$<2.1 \times 10^{-6}$	
Thallium	$<4.6 \times 10^{-4}$		$<4.1 \times 10^{-6}$	
Thorium	1.1×10^{-3}		1.0×10^{-5}	
Thullium	$<2.3 \times 10^{-4}$		$<2.1 \times 10^{-6}$	
Tin	0.15	$\{6.5 \times 10^{-2}\}$	1.4×10^{-3}	$\{6.2 \times 10^{-6}\}$
Titanium	3.1×10^{-2}	$\{9.8 \times 10^{-3}\}$	2.9×10^{-4}	$\{8.9 \times 10^{-5}\}$
Tungsten	6.8×10^{-3}		6.2×10^{-6}	
Uranium	$<2.3 \times 10^{-4}$		$<2.1 \times 10^{-6}$	
Vanadium	4.6×10^{-4}	$\{1.4 \times 10^{-2}\}$	4.1×10^{-6}	$\{1.2 \times 10^{-4}\}$
Ytterbium	6.9×10^{-4}		6.2×10^{-6}	
Yttrium	6.9×10^{-4}		6.2×10^{-6}	
Zinc	2.5	{0.16}	2.3×10^{-2}	$\{1.4 \times 10^{-3}\}$
Zirconium	1.3×10^{-2}		1.2×10^{-4}	
TOTAL Trace Elements[c]	18.4	{17.5}	0.17	{0.16}

[a] Not detected at 1 ppm.

[b] Values in braces ({}) were determined by ICAP with the exception of those for arsenic, mercury, and selenium, which were determined by atomic absorption. Values not in braces were determined by SSMS.

[c] Totals do not include numbers recorded as upper bounds.

Table F-3. EMISSIONS DATA FROM RUN 4-TM

Emission	Concentration, mg/m^3	Emission factor, g/kg
Inert gases		
Nitrogen	930,580	10,460
Oxygen	22,250	250
Carbon dioxide	62,985	710
Water	528,260	5,940
Criteria pollutants		
Particulate matter	7.5	0.083
Sulfur oxides	_[a]	_[a]
Nitrogen oxides	24	0.27
Hydrocarbons	3,190	35
Carbon monoxide	138,570	1,560
Chemical substances		
Hydrogen	_[b]	_[b]
Hydrogen sulfide	2,085	23
Carbon disulfide	3,390	30
Carbonyl sulfide	950	9
Methane	1,785	20
Acetylene	3,180	35
Ethylene	63	0.71
Propylene	_[a]	_[a]
Propane	10	0.12
Isobutane	5	0.06
n-Butane	17	0.19
Trace elements[c]		
Aluminum	0.15 {0.27}	1.7×10^{-3} {3.0×10^{-3}}
Antimony	9.5×10^{-4} {5.5×10^{-2}}	1.1×10^{-5} {6.2×10^{-4}}
Arsenic	$<2.3 \times 10^{-3}$ {5.0×10^{-3}}	$<2.5 \times 10^{-5}$ {5.6×10^{-6}}
Barium	6.1×10^{-3} {0.10}	6.8×10^{-5} {1.2×10^{-3}}
Beryllium	$<1.9 \times 10^{-4}$	$<2.2 \times 10^{-6}$
Bismuth	$<1.5 \times 10^{-3}$	$<1.8 \times 10^{-5}$
Boron	{0.7}	{7.8×10^{-3}}
Bromine	7.6×10^{-4}	8.9×10^{-6}

(continued)

Table F-3 (continued). EMISSIONS DATA FROM RUN 4-TM

Emission	Concentration, mg/m^3		Emission factor, g/kg	
Cadmium	5.7×10^{-4}	$\{2.8 \times 10^{-3}\}$	8.5×10^{-6}	$\{3.2 \times 10^{-5}\}$
Calcium	2.3	{3.5}	2.7×10^{-2}	$\{4.0 \times 10^{-2}\}$
Cerium	$<3.8 \times 10^{-4}$		$<4.5 \times 10^{-6}$	
Cesium	$<1.9 \times 10^{-4}$		$<2.2 \times 10^{-6}$	
Chlorine	0.72		1.2×10^{-3}	
Chromium	1.7×10^{-2}	$\{2.3 \times 10^{-3}\}$	2.0×10^{-4}	$\{2.6 \times 10^{-5}\}$
Cobalt	3.4×10^{-3}	$\{7.2 \times 10^{-3}\}$	4.0×10^{-5}	$\{8.1 \times 10^{-5}\}$
Copper	0.4	{0.23}	4.7×10^{-3}	$\{2.6 \times 10^{-3}\}$
Dysprosium	$<1.9 \times 10^{-4}$		$<2.2 \times 10^{-6}$	
Erbium	7.6×10^{-4}		8.9×10^{-6}	
Europium	$<5.7 \times 10^{-4}$		$<6.7 \times 10^{-6}$	
Fluorine	0.25		2.9×10^{-3}	
Gadolinium	2.5×10^{-3}		2.9×10^{-5}	
Gallium	$<1.9 \times 10^{-4}$		$<2.2 \times 10^{-6}$	
Germanium	$<1.9 \times 10^{-4}$		$<2.2 \times 10^{-6}$	
Gold	$<1.9 \times 10^{-4}$		$<2.2 \times 10^{-6}$	
Hafnium	1.5×10^{-3}		1.8×10^{-5}	
Holmium	$<1.9 \times 10^{-4}$		$<2.2 \times 10^{-6}$	
Iodine	$<5.7 \times 10^{-4}$		$<6.7 \times 10^{-6}$	
Iridium	$<3.8 \times 10^{-4}$		$<4.5 \times 10^{-6}$	
Iron	0.18	{0.43}	2.1×10^{-3}	$\{4.7 \times 10^{-3}\}$
Lanthanum	3.8×10^{-4}		4.5×10^{-6}	
Lead	0.19	$\{5.5 \times 10^{-2}\}$	2.2×10^{-3}	$\{6.2 \times 10^{-4}\}$
Lithium	$<1.9 \times 10^{-4}$		$<2.2 \times 10^{-6}$	
Lutecium	$<3.8 \times 10^{-4}$		$<4.5 \times 10^{-6}$	
Magnesium	1.8	{0.38}	2.1×10^{-2}	$\{4.3 \times 10^{-3}\}$
Manganese	1.0×10^{-2}	$\{7.5 \times 10^{-3}\}$	5.3×10^{-4}	$\{8.5 \times 10^{-5}\}$
Mercury		$\{2.7 \times 10^{-3}\}$		$\{3.1 \times 10^{-5}\}$
Molybdenum	1.0×10^{-2}	$\{9.4 \times 10^{-3}\}$	5.3×10^{-4}	$\{7.0 \times 10^{-4}\}$
Neodymium	$<3.8 \times 10^{-4}$		$<4.5 \times 10^{-6}$	
Nickel	6.6×10^{-2}	{0.11}	7.7×10^{-4}	$\{1.2 \times 10^{-3}\}$
Niobium	$<5.7 \times 10^{-4}$		$<6.7 \times 10^{-6}$	
Osmium	$<5.7 \times 10^{-4}$		$<6.7 \times 10^{-6}$	
Palladium	$<3.8 \times 10^{-4}$		$<4.5 \times 10^{-6}$	
Phosphorus	0.19	{0.13}	2.3×10^{-3}	$\{1.5 \times 10^{-2}\}$

(continued)

Table F-3 (continued). EMISSIONS DATA FROM RUN 4-TM

Emission	Concentration, mg/m^3		Emission factor, g/kg	
Platinum	$<5.7 \times 10^{-4}$		$<6.7 \times 10^{-6}$	
Potassium	2.3		2.7×10^{-2}	
Praseodymium	$<3.8 \times 10^{-4}$		$<4.5 \times 10^{-6}$	
Rhodium	$<1.9 \times 10^{-4}$		$<2.2 \times 10^{-6}$	
Rubidium	3.2×10^{-3}		3.8×10^{-5}	
Samarium	$<1.9 \times 10^{-3}$		$<2.2 \times 10^{-6}$	
Scandium	$<3.8 \times 10^{-4}$		$<4.5 \times 10^{-6}$	
Selenium	$<3.8 \times 10^{-4}$	$\{1.9 \times 10^{-4}\}$	$<4.5 \times 10^{-6}$	$\{2.0 \times 10^{-6}\}$
Silicon	2.9	{1.2}	3.5×10^{-2}	$\{1.4 \times 10^{-2}\}$
Sodium	4.3	{2.3}	5.1×10^{-2}	$\{2.6 \times 10^{-2}\}$
Strontium	5.7×10^{-2}	$\{1.3 \times 10^{-2}\}$	6.7×10^{-4}	$\{1.5 \times 10^{-4}\}$
Tantalum	$<9.5 \times 10^{-4}$		1.1×10^{-5}	
Terbium	$<1.9 \times 10^{-4}$		$<2.2 \times 10^{-6}$	
Tellurium	$<1.9 \times 10^{-4}$		$<2.2 \times 10^{-6}$	
Thallium	$<5.7 \times 10^{-4}$		$<6.7 \times 10^{-6}$	
Thorium	1.5×10^{-3}		1.8×10^{-5}	
Thullium	$<3.8 \times 10^{-4}$		$<4.5 \times 10^{-6}$	
Tin	0.13	{0.13}	1.5×10^{-3}	$\{1.5 \times 10^{-3}\}$
Titanium	1.3×10^{-2}	$\{8.7 \times 10^{-3}\}$	1.6×10^{-4}	$\{1.0 \times 10^{-4}\}$
Tungsten	2.3×10^{-3}		2.7×10^{-5}	
Uranium	$<9.5 \times 10^{-4}$		$<1.1 \times 10^{-5}$	
Vanadium	7.6×10^{-4}	$\{9.4 \times 10^{-3}\}$	8.9×10^{-6}	$\{1.0 \times 10^{-5}\}$
Ytterbium	7.6×10^{-4}		8.9×10^{-6}	
Yttrium	3.8×10^{-4}		$<4.5 \times 10^{-6}$	
Zinc	3.4	{0.37}	4.0×10^{-2}	$\{4.1 \times 10^{-3}\}$
Zirconium	6.6×10^{-3}		7.8×10^{-5}	
TOTAL Trace elements[d]	19.4	{14.2}	0.22	{0.15}

[a] Not detected at 1 ppm.

[b] Sample thrown out; too low.

[c] Values in braces ({}) were determined by ICAP with the exception of those for arsenic, mercury, and selenium, which were determined by atomic absorption. Values not in braces were determined by SSMS.

[d] Totals do not include numbers recorded as upper bounds.

Table F-4. EMISSIONS DATA FROM RUN POM-1

Emission	Concentration, mg/m^3	Emission factor, g/kg
Inert gases		
Nitrogen	778,730	7,630
Oxygen	70,675	690
Carbon dioxide	52,190	510
Water	581,035	5,695
Criteria pollutants		
Particulate matter	-^{a}	-^{a}
Sulfur oxides	-^{b}	-^{b}
Nitrogen oxides	25	0.25
Hydrocarbons	3,762	37
Carbon monoxide	104,210	1,020
Chemical substances		
Hydrogen	11,940	117
Hydrogen sulfide	2,055	20
Carbon disulfide	2,690	26
Carbonyl sulfide	785	8
Methane	1,825	18
Acetylene	3,575	35
Ethylene	146	1.4
Propylene	-^{b}	-^{b}
Propane	15	0.15
Isobutane	7	0.07
n-Butane	26	0.25
POM		
Acenaphthylene	4.7×10^{-2}	4.7×10^{-4}
Anthracene/phenanthrene	3.5×10^{-3}	3.5×10^{-5}
Benzo[c]phenanthrene	2.2×10^{-4}	2.2×10^{-6}
Benzofluoranthenes	4.4×10^{-3}	4.3×10^{-5}
Benzo[ghi]fluoranthene	2.6×10^{-3}	2.6×10^{-5}

(continued)

Table F-4 (continued). EMISSIONS DATA FROM RUN POM-1

Emission	Concentration, mg/m^3	Emission factor, g/kg
Benzo[ghi]perylene/anthanthrene	1.3×10^{-3}	1.3×10^{-5}
Benzopyrenes/perylene	3.1×10^{-3}	3.0×10^{-5}
Chrysene/benz[a]anthracene	8.7×10^{-4}	8.5×10^{-6}
Dibenzanthracenes	$<1.1 \times 10^{-4}$	$<1.0 \times 10^{-6}$
Dibenzo[c,g]carbazole	$<1.1 \times 10^{-4}$	$<1.0 \times 10^{-6}$
Dibenzopyrenes	$<1.1 \times 10^{-4}$	$<1.0 \times 10^{-6}$
Dibenzothiophene	3.3×10^{-4}	3.3×10^{-5}
Dimethylanthracene/phenanthrene	8.4×10^{-3}	8.2×10^{-5}
7,12-Dimethylbenz[a]anthracene	1.1×10^{-2}	1.1×10^{-4}
Fluoranthene	3.1×10^{-3}	3.0×10^{-5}
Indeno[1,2,3-cd]pyrene	$<1.1 \times 10^{-4}$	$<1.0 \times 10^{-6}$
Methylanthracene	7.5×10^{-3}	7.4×10^{-5}
Methylcholanthrene	$<1.1 \times 10^{-4}$	$<1.0 \times 10^{-6}$
Methylfluoranthene	2.3×10^{-3}	2.2×10^{-5}
Pyrene	2.6×10^{-2}	2.6×10^{-4}
TOTAL POM[c]	1.2×10^{-1}	1.2×10^{-3}

[a] Not determined.

[b] Not detected at 1 ppm.

[c] Total does not include numbers recorded as upper bounds.

Table F-5. EMISSIONS DATA FROM RUN POM-2

Emission	Concentration, mg/m^3	Emission factor, g/kg
Inert gases		
Nitrogen	794,800	10,505
Oxygen	6,020	80
Carbon dioxide	64,785	855
Water	605,970	8,010
Criteria pollutants		
Particulate matter	—[a]	—[a]
Sulfur oxides	—[b]	—[b]
Nitrogen oxides	27	0.35
Hydrocarbons	5,997	79
Carbon monoxide	135,130	1,785
Chemical substances		
Hydrogen	11,950	160
Hydrogen sulfide	4,775	63
Carbon disulfide	12,420	164
Carbonyl sulfide	2,375	31
Methane	3,028	40
Acetylene	5,705	75
Ethylene	237	3.1
Propylene	—[b]	—[b]
Propane	24	0.47
Isobutane	13	0.18
n-Butane	31	0.41
POM		
Acenaphthylene	1.0×10^{-1}	1.4×10^{-3}
Anthracene/phenanthrene	9.4×10^{-3}	1.2×10^{-4}
Benzo[c]phenanthrene	1.7×10^{-4}	2.2×10^{-6}
Benzofluoranthenes	3.1×10^{-3}	4.1×10^{-5}
Benzo[ghi]fluoranthene	5.2×10^{-3}	6.8×10^{-5}

(continued)

Table F-5 (continued). EMISSIONS DATA FROM RUN POM-2

Emission	Concentration, mg/m^3	Emission factor, g/kg
Benzo[ghi]perylene/anthanthrene	2.8×10^{-3}	3.8×10^{-5}
Benzopyrenes/perylene	2.8×10^{-3}	3.8×10^{-5}
Chrysene/benz[a]anthracene	7.9×10^{-4}	1.0×10^{-5}
Dibenzanthracenes	$<1.6 \times 10^{-4}$	$<2.1 \times 10^{-6}$
Dibenzo[c,g]carbazole	$<1.6 \times 10^{-4}$	$<2.1 \times 10^{-6}$
Dibenzopyrenes	$<1.6 \times 10^{-4}$	$<2.1 \times 10^{-6}$
Dibenzothiophene	1.8×10^{-3}	2.4×10^{-5}
Dimethylanthracene/phenanthrene	1.7×10^{-2}	2.2×10^{-4}
7,12-Dimethylbenz[a]anthracene	4.2×10^{-3}	5.6×10^{-5}
Fluoranthene	7.9×10^{-3}	1.1×10^{-4}
Indeno[1,2,3-cd]pyrene	$<1.6 \times 10^{-4}$	$<2.1 \times 10^{-6}$
Methylanthracene	1.1×10^{-2}	1.4×10^{-4}
Methylcholanthrene	$<1.6 \times 10^{-4}$	$<2.1 \times 10^{-6}$
Methylfluoranthene	2.5×10^{-3}	3.3×10^{-5}
Pyrene	5.6×10^{-2}	7.4×10^{-4}
TOTAL POM[c]	2.2×10^{-1}	3.0×10^{-3}

[a] Not determined.

[b] Not detected at 1 ppm.

[c] Total does not include numbers recorded as upper bounds.

Table F-6. EMISSIONS DATA FROM RUN POM-3

Emission	Concentration, mg/m^3	Emission factor, g/kg
Inert gases		
Nitrogen	794,800	7,880
Oxygen	6,020	60
Carbon dioxide	64,785	665
Water	589,690	6,050
Criteria pollutants		
Particulate matter	–[a]	–[a]
Sulfur oxides	–[b]	–[b]
Nitrogen oxides	24	0.25
Hydrocarbons	–[a]	–[b]
Carbon monoxide	135,130	1,385
Chemical substances		
Hydrogen	–[a]	–[a]
Hydrogen sulfide	–[a]	–[a]
Carbon disulfide	–[a]	–[a]
Carbonyl sulfide	–[a]	–[a]
Methane	–[a]	–[a]
Acetylene	–[a]	–[a]
Ethylene	–[a]	–[a]
Propylene	–[a]	–[a]
Propane	–[a]	–[a]
Isobutane	–[a]	–[a]
n-Butane	–[a]	–[a]
POM		
Acenaphthylene	6.7×10^{-2}	6.9×10^{-4}
Anthracene/phenanthrene	4.6×10^{-3}	4.8×10^{-5}
Benzo[c]phenanthrene	1.6×10^{-4}	1.6×10^{-6}
Benzofluoranthenes	1.2×10^{-3}	1.3×10^{-5}
Benzo[ghi]fluoranthene	9.9×10^{-4}	1.0×10^{-5}

(continued)

Table F-6 (continued). EMISSIONS DATA FROM RUN POM-3

Emission	Concentration, mg/m^3	Emission factor, g/kg
Benzo[ghi]perylene/anthanthrene	1.9×10^{-3}	1.9×10^{-5}
Benzopyrenes/perylene	8.6×10^{-4}	8.8×10^{-6}
Chrysene/benz[a]anthracene	6.9×10^{-4}	7.1×10^{-6}
Dibenzanthracenes	$<1.5 \times 10^{-4}$	$<1.6 \times 10^{-6}$
Dibenz[c,g]carbazole	$<1.5 \times 10^{-4}$	$<1.6 \times 10^{-6}$
Dibenzopyrenes	$<1.5 \times 10^{-4}$	$<1.6 \times 10^{-6}$
Dibenzothiophene	1.5×10^{-3}	1.5×10^{-5}
Dimethylanthracene/phenanthrene	1.1×10^{-2}	1.1×10^{-4}
7,12-Dimethylbenz[a]anthracene	4.7×10^{-3}	4.8×10^{-5}
Fluoranthene	3.7×10^{-3}	3.8×10^{-5}
Indeno[1,2,3-cd]pyrene	$<1.5 \times 10^{-4}$	$<1.6 \times 10^{-6}$
Methylanthracene	6.7×10^{-3}	6.9×10^{-5}
Methylchlolanthrene	$<1.5 \times 10^{-4}$	$<1.6 \times 10^{-6}$
Methylfluoranthene	1.4×10^{-3}	1.4×10^{-5}
Pyrene	3.7×10^{-2}	3.7×10^{-4}
TOTAL POM[c]	1.4×10^{-1}	1.5×10^{-3}

[a] Not determined.

[b] Not detected at 1 ppm.

[c] Total does not include numbers recorded as upper bounds.

Table F-7. COMPARISON OF TRACE ELEMENT RUNS WITH BLANK RUN: SSMS ANALYSIS ($C_1 + C_2$, mg/ℓ)[a]

Element	Run			
	1-TM	3-TM	4-TM	5-TM (blank)
Aluminum	1.8	1.2	0.8	2.5
Antimony	0.039	0.008	0.005	<0.005
Arsenic[b]	0.038	0.021	0.027	0.015
Barium	2.9	1.5	0.03	1.4
Beryllium	<0.003	<0.002	<0.002	<0.003
Bismuth	<0.011	<0.003	<0.009	<0.011
Bromine	0.008	0.003	<0.005	<0.006
Cadmium	0.016	0.007	0.004	<0.003
Calcium	42	22	12	79
Cerium	0.003	0.003	0.003	<0.003
Cesium	<0.002	<0.002	<0.002	0.005
Chlorine	5.0	0.09	3.9	14.2
Chromium	0.57	0.15	0.091	0.076
Cobalt	0.11	0.081	0.019	0.005
Copper	20	1.3	2.1	0.51
Dysprosium	<0.003	<0.002	<0.002	<0.002
Erbium	<0.008	<0.005	<0.005	<0.007
Europium	<0.004	<0.003	<0.004	<0.004
Fluorine	0.68	1.2	1.3	0.90
Gadolinium	<0.007	<0.013	<0.013	<0.018
Gallium	<0.002	<0.002	<0.002	<0.002
Germanium	<0.003	<0.002	<0.002	<0.003
Gold	<0.003	<0.002	<0.002	<0.003
Hafnium	<0.013	<0.007	<0.008	<0.010
Holmium	<0.003	<0.002	<0.002	<0.003
Iodine	<0.004	<0.002	<0.004	<0.004
Iridium	<0.004	<0.003	<0.003	<0.004
Iron	5.0	2.7	0.95	2.2
Lanthanum	0.003	0.002	<0.003	<0.003
Lead	0.61	0.76	0.98	0.29
Lithium	0.023	0.004	NR[c]	0.004
Lutecium	<0.003	<0.002	<0.003	<0.003
Magnesium	27	4.6	9.4	2.7
Manganese	0.18	0.034	0.055	0.073
Mercury[b]	0.0015	0.205	0.011	<0.0004
Molybdenum	0.083	0.097	0.054	0.04
Neodymium	<0.004	<0.003	<0.003	<0.003
Nickel	1.4	0.72	0.35	0.09
Niobium	<0.004	<0.002	<0.004	<0.004
Osmium	<0.005	<0.004	<0.003	<0.005
Palladium	<0.004	<0.003	<0.003	<0.004
Phosphorus	14	0.30	1.0	13
Platinum	<0.005	<0.004	<0.004	<0.005

(continued)

Table F-7 (continued). COMPARISON OF TRACE ELEMENT RUNS WITH BLANK RUN: SSMS ANALYSIS

	Run			
Element	1-TM	3-TM	4-TM	5-TM (blank)
Potassium	38.2	6.3	12	36
Praseodymium	<0.004	<0.002	<0.003	<0.004
Rhodium	0.002	<0.002	<0.002	<0.002
Rubidium	0.009	0.006	0.018	0.002
Samarium	0.014	<0.002	<0.011	<0.013
Scandium	<0.004	<0.003	<0.003	<0.004
Selenium[b]	<0.002	<0.002	<0.002	<0.002
Silicon	8.3	6.1	13.3	9.0
Sodium	29	19	23	9.2
Strontium	0.077	0.043	0.30	0.042
Tantalum	<0.017	<0.002	<0.006	<0.007
Terbium	<0.002	<0.002	<0.002	<0.002
Tellurium	<0.003	<0.002	<0.002	<0.003
Thallium	<0.005	<0.003	<0.004	<0.005
Thorium	<0.011	<0.005	<0.009	<0.012
Thullium	<0.004	<0.002	<0.003	<0.004
Tin	0.87	0.68	0.67	0.24
Titanium	0.070	0.135	0.070	0.013
Tungsten	<0.018	<0.004	<0.013	<0.017
Uranium	<0.007	<0.002	<0.006	<0.007
Vanadium	0.017	0.003	0.005	0.017
Ytterbium	<0.009	<0.004	<0.005	<0.006
Yttrium	0.008	0.004	0.003	0.005
Zinc	63	11	18	130
Zirconium	0.066	0.058	0.035	0.018

[a] C_1 = concentration in sample from front half of sampling train; C_2 = concentration in sample from back half of sampling train. All sample volumes were 250 mℓ.

[b] Determined by atomic absorption.

[c] Not reported.

Table F-8. COMPARISON OF TRACE ELEMENT RUNS WITH BLANK RUN: ICAP ANALYSIS (C_1 + C_2, mg/ℓ)[a]

Element	Run			
	1-TM	3-TM	4-TM	5-TM (blank)
Aluminum	2.0	1.7	1.4	1.4
Antimony	0.084	0.11	0.29	0.12
Barium	0.87	0.59	0.57	0.42
Boron	3.2	3.0	3.7	1.2
Calcium	54	43	19	60
Cadmium	0.043	0.030	0.015	0.013
Cobalt	0.040	0.050	0.038	0.047
Chromium	0.13	0.060	0.12	0.034
Copper	4.4	0.46	1.2	0.20
Iron	3.3	1.5	2.3	0.59
Lead	0.58	0.41	0.28	0.22
Magnesium	1.5	2.4	2.0	0.82
Manganese	0.048	0.031	0.040	0.013
Molybdenum	0.083	0.070	0.050	0.043
Nickel	0.47	0.74	0.56	0.72
Phosphorus	1.4	0.68	0.69	0.60
Silicon	3.6	3.0	6.5	6.4
Sodium	15	10	12	5.7
Strontium	0.061	0.042	0.071	0.042
Tin	0.49	0.30	0.69	0
Titanium	0.045	0.043	0.046	0.024
Vanadium	0.055	0.060	0.050	0.053
Zinc	8.7	7.7	1.9	11

[a] C_1 = concentration in sample from front half of sampling train; C_2 = concentration in sample from back half of sampling train. All sample volumes were 250 mℓ.

APPENDIX G

SIMULATED SOURCE SEVERITY DISTRIBUTIONS

Simulated source severity distributions are presented in Figures G-1 through G-22. These distributions were computed according to the methodology set forth in Reference 41. Due to the large number of emission species associated with this source type, distributions are shown only for those emissions for which the representative plant source severity is 0.1 or greater.

Input data to the simulation routine consisted of stack heights and production rates taken from the survey of operating plants in Reference 21, and emission factors from Table 31. For the purpose of this simulation, the carbon black industry is considered to be homogeneous with respect to emissions. That is, variability in emission factors is due only to process variability and variability in sampling and analytical procedures; no plant-to-plant variability is assumed. This assumption is consistent with the sampling strategy employed in this study, i.e., only one plant was sampled. Thus, emission factors were assumed to be normally distributed with parameters determined by the means and 95% confidence limits listed in Table 31. Furthermore, the simulated source severities were computed assuming no plume rise and no combustion devices used to burn the main process vent gas.

In Figures G-1 through G-22, the ordinate, labelled "cumulative frequency," should be interpreted as the percentage of plants which have a severity less than the corresponding value on the abscissa.

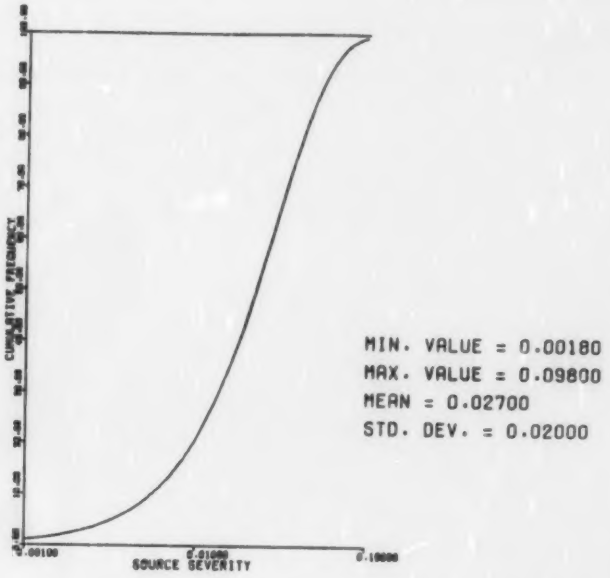


Figure G-1. Simulated source severity distribution for particulate emissions from main process vent

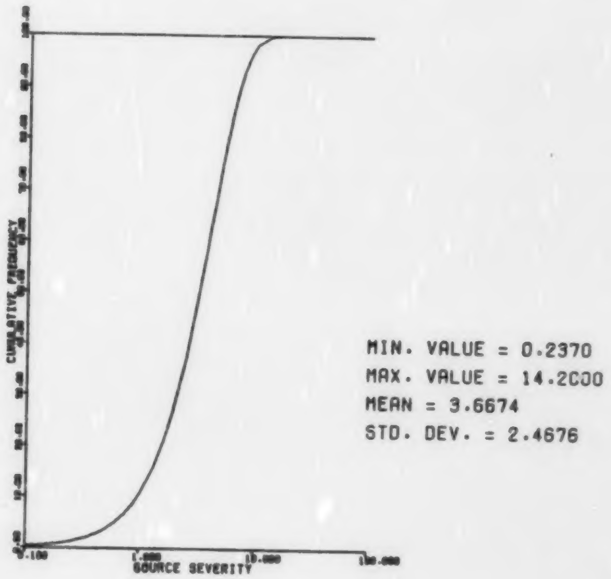


Figure G-2. Simulated source severity distribution for carbon monoxide emissions from main process vent

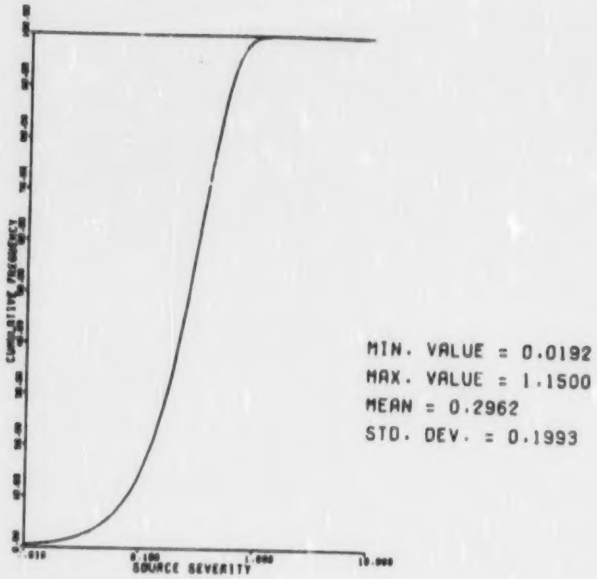


Figure G-3. Simulated source severity distribution for nitrogen oxide emissions from main process vent

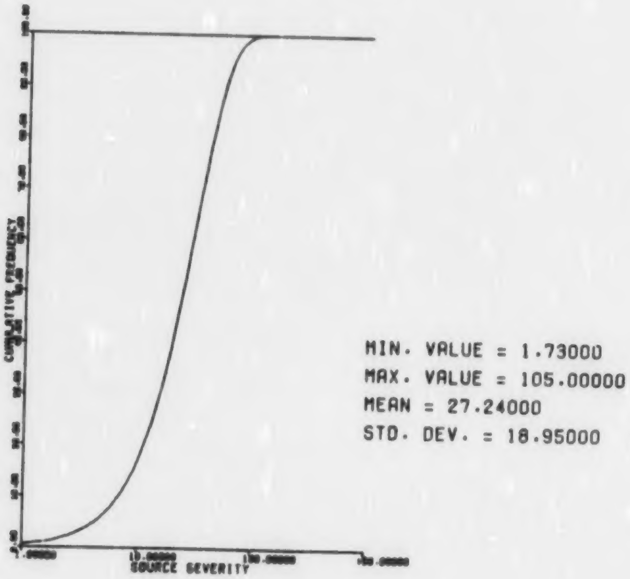


Figure G-4. Simulated source severity distribution for hydrocarbon emissions from main process vent

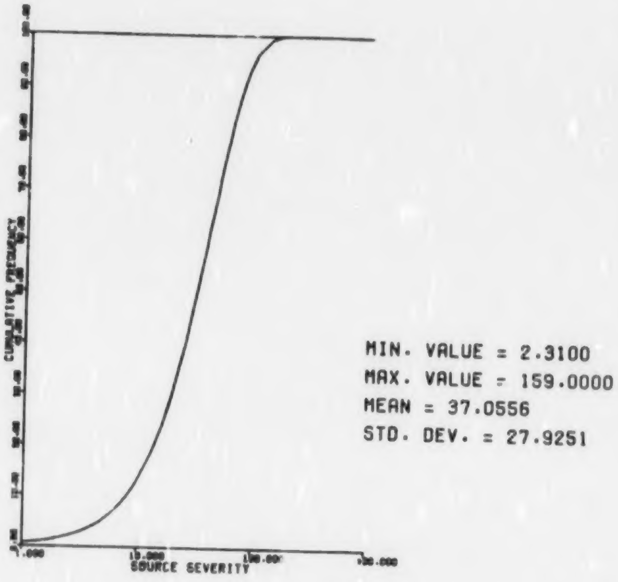


Figure G-5. Simulated source severity distribution for hydrogen sulfide emissions from main process vent

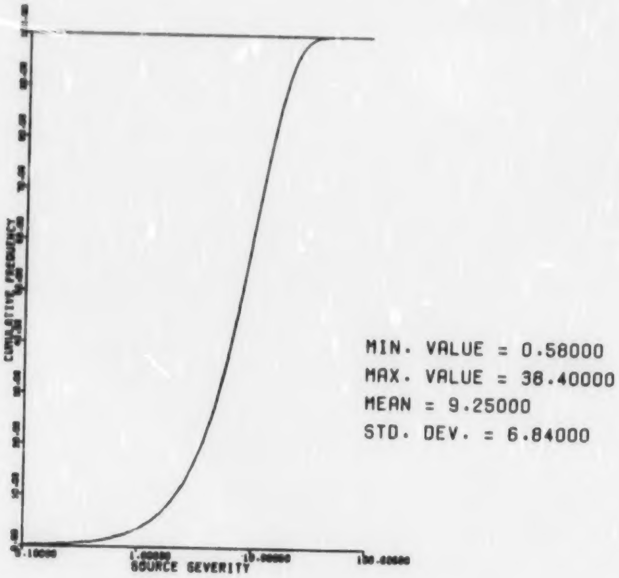


Figure G-6. Simulated source severity distribution for carbon disulfide emissions from main process vent

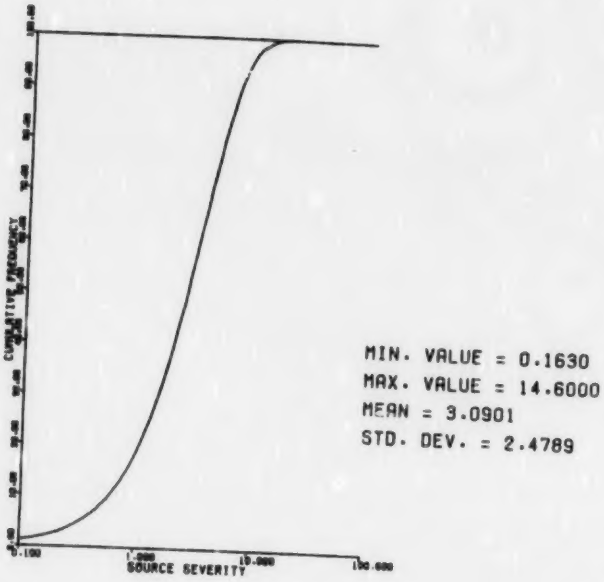


Figure G-7. Simulated source severity distribution for carbonyl sulfide emissions from main process vent

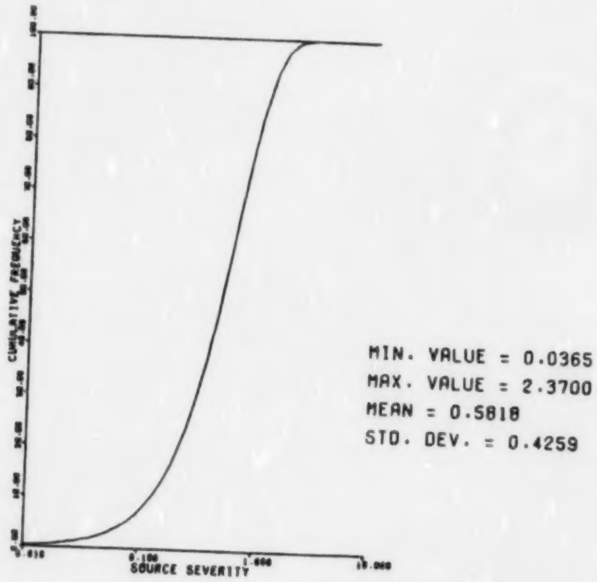
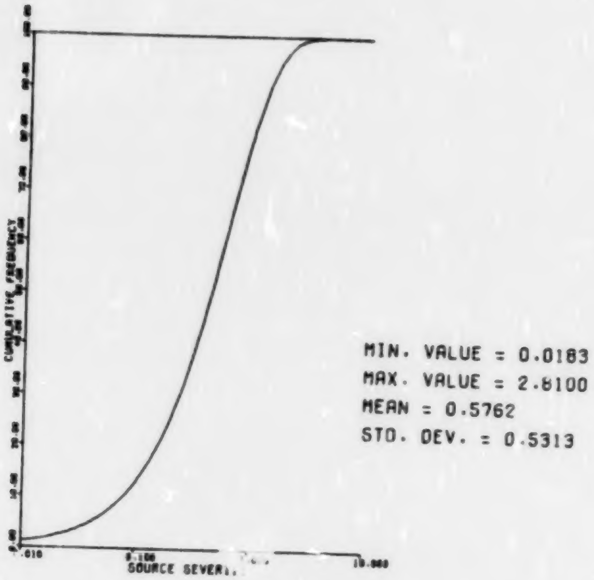
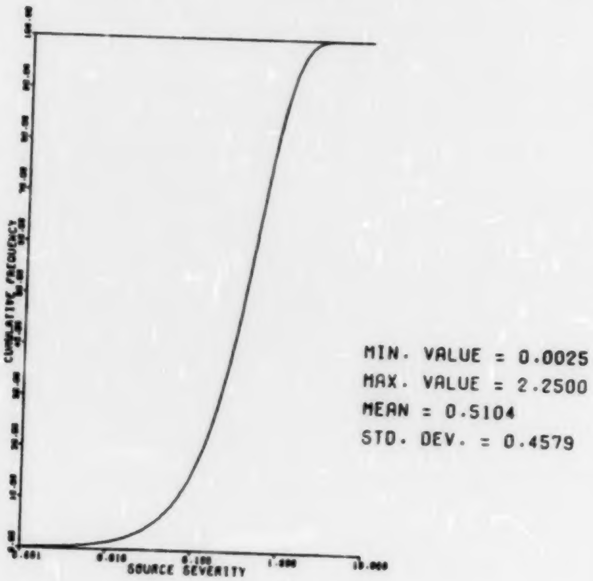


Figure G-8. Simulated source severity distribution for carbon black emissions from main process vent



MIN. VALUE = 0.0183
MAX. VALUE = 2.8100
MEAN = 0.5762
STD. DEV. = 0.5313

Figure G-9. Simulated source severity distribution for benzofluoranthene emissions from main process vent



MIN. VALUE = 0.0025
MAX. VALUE = 2.2500
MEAN = 0.5104
STD. DEV. = 0.4579

Figure G-10. Simulated source severity distribution for benzopyrene emissions from main process vent

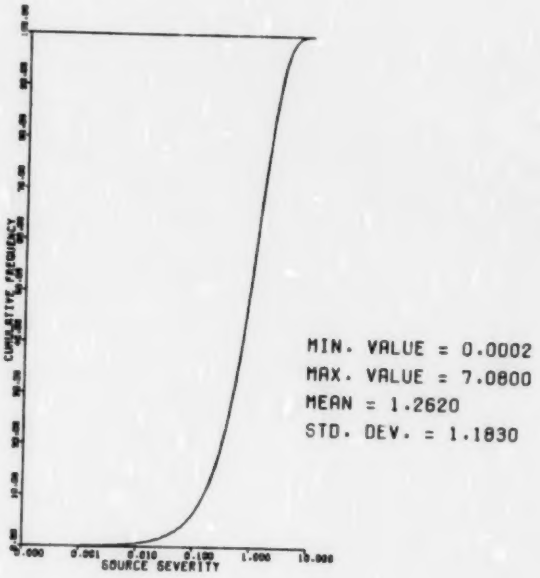


Figure G-11. Simulated source severity distribution for 7,12-Dimethylbenz[a]anthracene emissions from main process vent

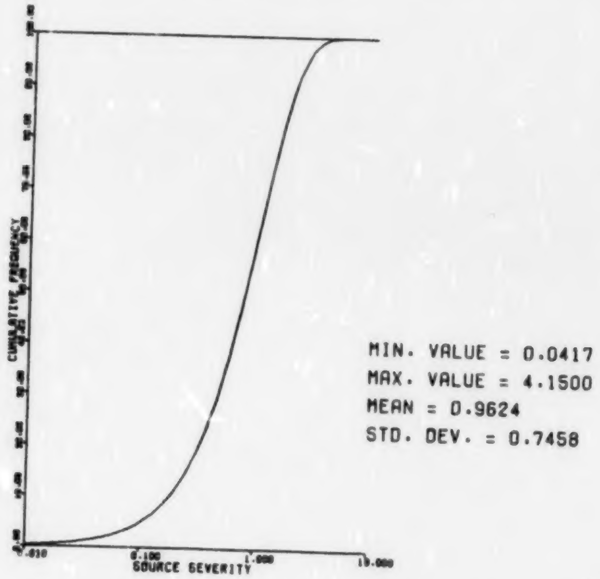


Figure G-12. Simulated source severity distribution for copper emissions from main process vent

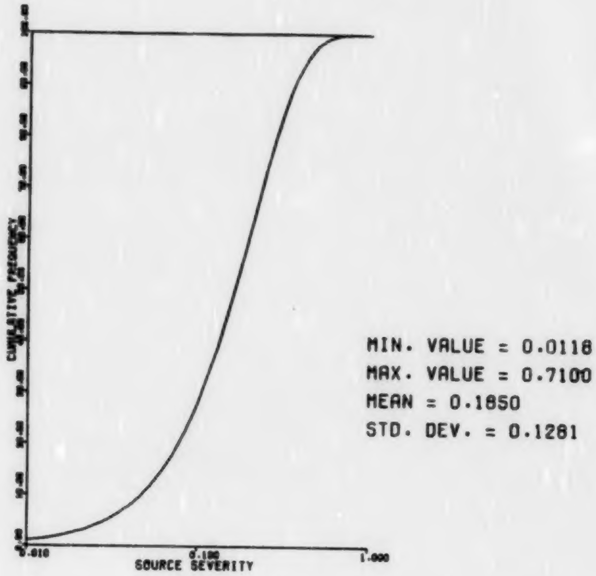


Figure G-13. Simulated source severity distribution for lead emissions from main process vent

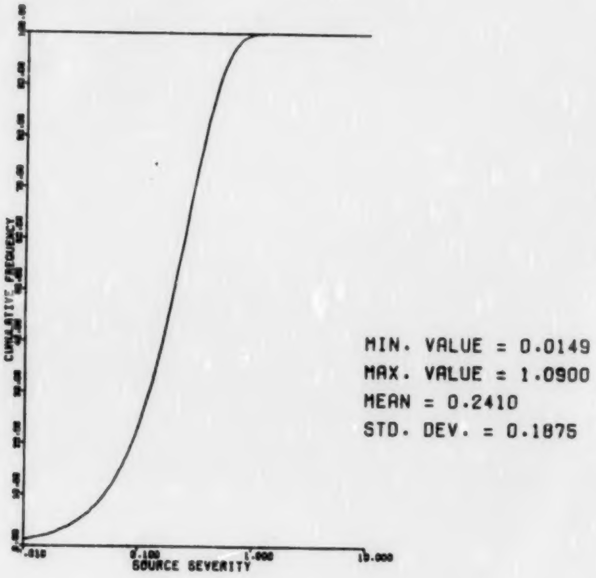


Figure G-14. Simulated source severity distribution for nickel emissions from main process vent

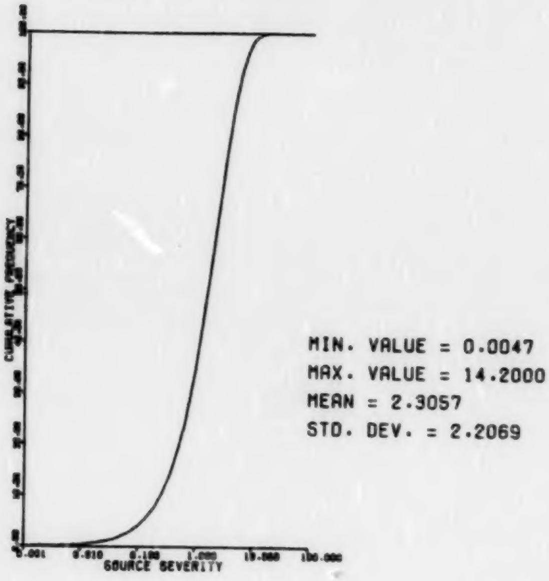


Figure G-15. Simulated source severity distribution for phosphorus emissions from main process vent

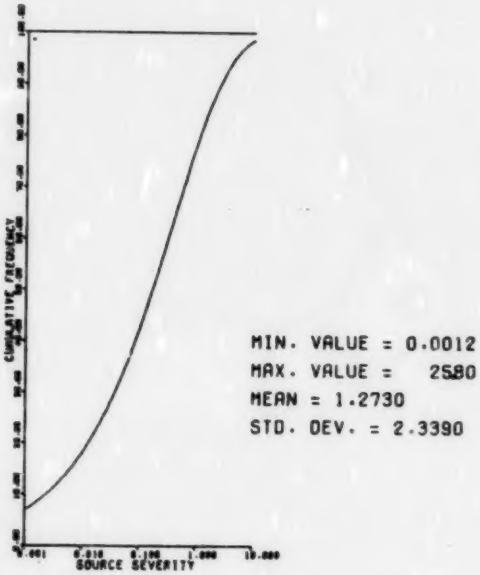


Figure G-16. Simulated source severity distribution for nitrogen oxide emissions from dryer vent

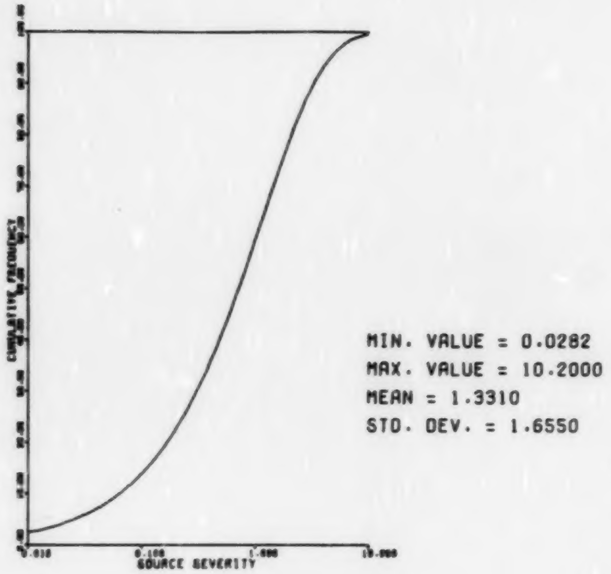


Figure G-17. Simulated source severity distribution for carbon black emissions from dryer vent

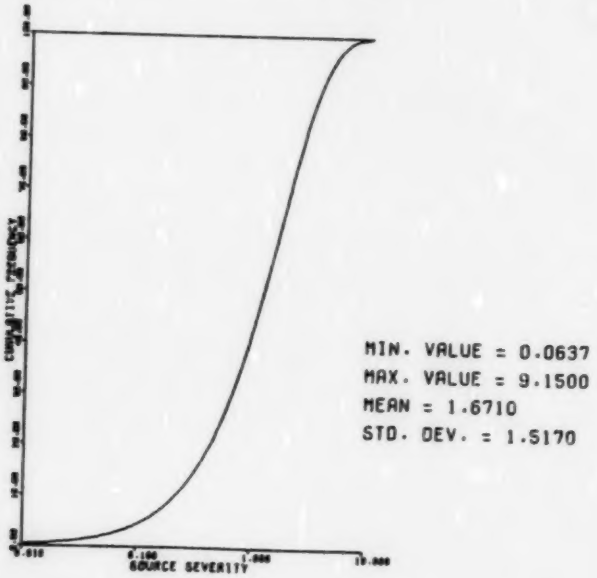


Figure G-18. Simulated source severity distribution for carbon black emissions from pneumatic system vent

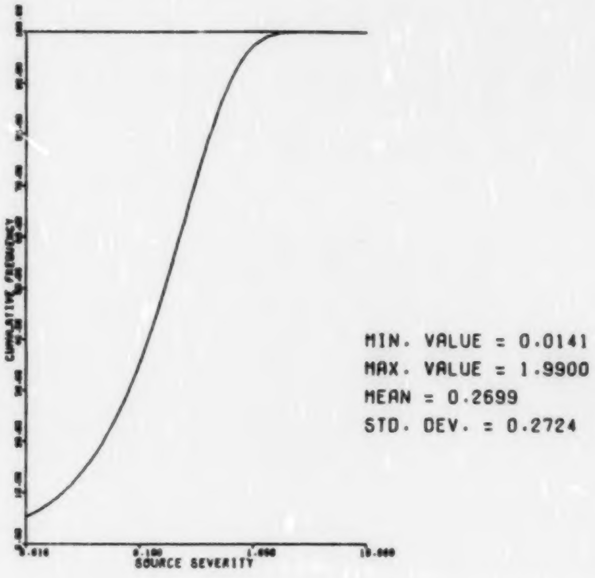


Figure G-19. Simulated source severity distribution for carbon black emissions from vacuum cleanup system vent

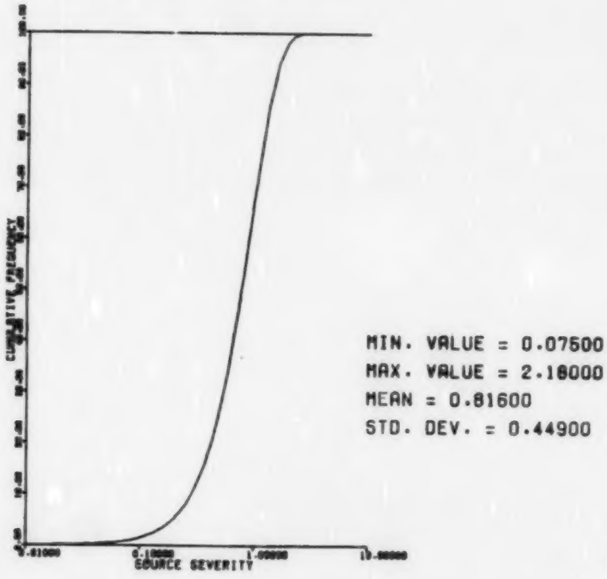


Figure G-20. Simulated source severity distribution for hydrocarbon emissions from oil storage tank vent

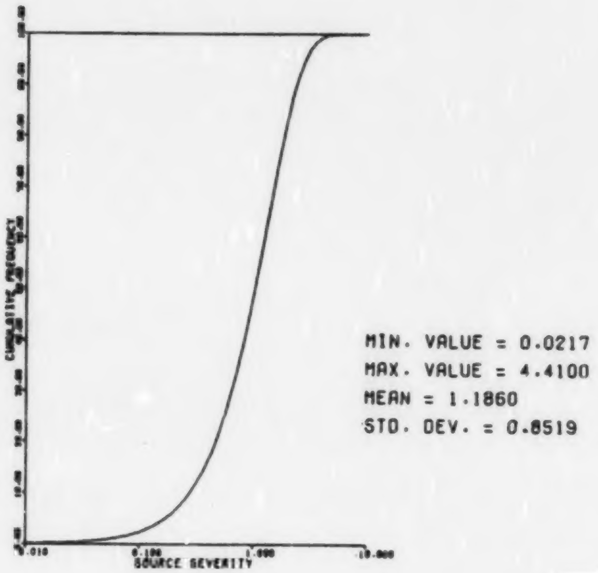


Figure G-21. Simulated source severity distribution for fugitive particulate emissions

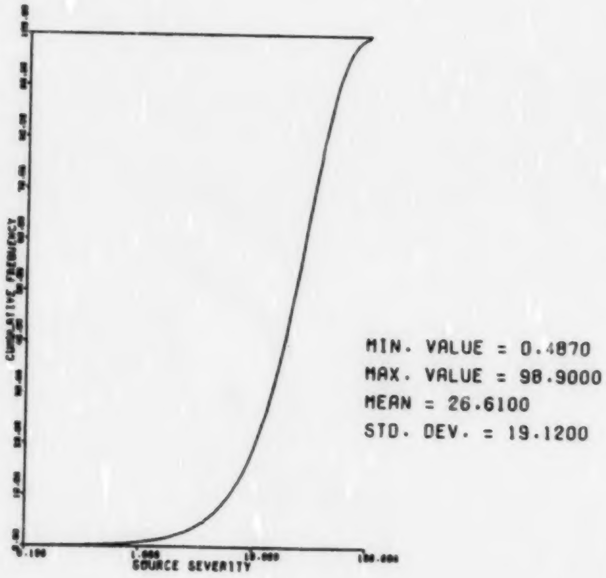


Figure G-22. Simulated source severity distribution for fugitive carbon black emissions

APPENDIX H

REMOTE MONITORING OF CARBON MONOXIDE IN FLARE OFF-GAS[a]

1. MONITORING EQUIPMENT AND PROCEDURES

The combustion efficiency of carbon monoxide in the flare was determined by measuring the CO concentration in the gas emitted from the flare stack using the ROSE (Remote Optical Sensing of Emissions) System.

Infrared energy radiated by the off-gases from the flare stack was collected by the ROSE system telescope and processed to display signal intensity as a function of wavelength (microns) or wave number (cm^{-1}). A block diagram of the ROSE System is shown in Figure H-1.[11] The field of view of the ROSE System through the flare was a rectangular section approximately 30 mm wide and 100 mm high. This rectangular section intersected the stack axis at about 0.5 m above the stack exit plane at an elevation angle of 30° as indicated in figure H-2. For analysis purposes, the assumptions were made that the off-gases were confined to a vertical cylinder with a diameter equal to that of the stack and that they were uniformly distributed along the line of sight within the cylinder.

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[a] This work was performed by EPA personnel under the direction of Dr. William F. Herget.

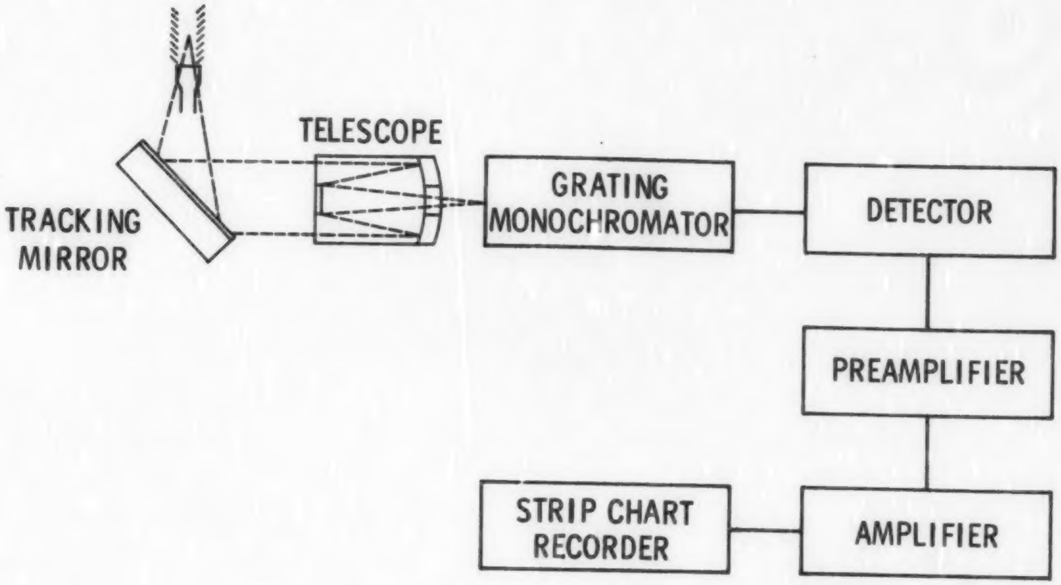
TELESCOPE
TRACKING MIRROR
GRATING MONOCHROMATOR
DETECTOR
PREAMPLIFIER
STRIP CHART RECORDER
AMPLIFIER

Figure H-1. Block diagram of ROSE System[11]

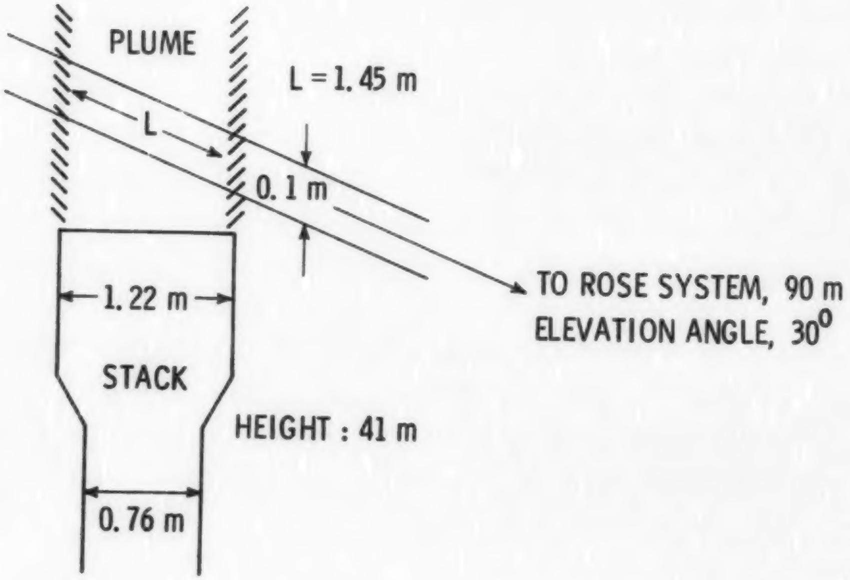
PLUME
L = 1.45 m
L
0.1 m
1.22 m
TO ROSE SYSTEM, 90 m
ELEVATION ANGLE, 30°
STACK
HEIGHT : 41 m
0.76 m

Figure H-2. Geometry of ROSE System measurements[11]

The basic equation for the calculation of species concentrations from the emission spectra are:

$$\varepsilon_\lambda = N_s(\lambda,\ T)\,[N_{bb}(\lambda,\ T)]^{-1}$$

$$\varepsilon_\lambda = 1 - e^{-K(\lambda,\ T)\hat{P}\hat{L}} \qquad \text{(H-1)}$$

where ε_λ = emissivity of the species at wavelength, λ

$N_s(\lambda,\ T)$ = spectral radiance of the species at wavelength, λ, and temperature, T

$N_{bb}(\lambda,\ T)$ = spectral radiance of a blackbody at wavelength, λ, and temperature, T

$K(\lambda,\ T)$ = spectral absorption coefficient of the species at λ and T

$\hat{P}$ = partial pressure of the species

$\hat{L}$ = optical path length in the plume

The two unknowns in these equations are T and $\hat{P}$. The quantity $K(\lambda,\ T)$ is determined in the laboratory from spectra obtained at known concentrations and temperatures or from theoretical calculations. The plume temperature can be calculated from an approximate knowledge of the CO_2 concentration and measurement of the CO_2 emission spectra at 2,275 cm^{-1} using the known spectral absorption coefficient for CO_2. The emissivity was calculated at 2,190 cm^{-1} by ratioing the spectral radiance of CO to that of a blackbody. Using the CO spectral absorption coefficient from the literature, Equation H-1 was used to calculate the CO partial pressure, and hence, its concentration.

2. ANALYTICAL PROCEDURE

The above equipment (EPA Rose System) and procedures used in the field measurements were identical to those used in a previous study.[11] To assist in the analysis of the field data, laboratory studies were carried out in a bunsen burner flame utilizing the "new" ROSE System. In the new system, the grating monochromator has been replaced by a Fourier Transform Spectrometer (FTS) capable of 0.06 cm^{-1} resolution. (The maximum resolution of the grating system was about 1.0 cm^{-1}.) It was thus possible to study the bunsen burner flame at high resolution and at a resolution comparable to that used in the field studies. but with a signal to noise ratio greater than that attainable with the grating system.

Figure H-3 shows spectra obtained with the FTX System and also field spectra. The uppermost spectrum (A) shows absorption due to atmospheric species and CO (combined in a cell). A composite of four spectra of the off-gas emission (with flare ignited) is shown also (B). Next is shown an emission spectrum of a bunsen burner flame (C) obtained with the FTS system; the lowermost spectrum (D) is from the same flame but with the field of view above the visible portion of the flame.

The spectral detail in (B) from approximately 2,156 cm^{-1} to 2,220 cm^{-1} was attributed to CO in the previous work.[11] Spectrum (C) shows, however, that if this detail were due to CO, it would also occur with similar intensities in the 2,004 cm^{-1} to 2,132 cm^{-1} region. Spectrum (B) actually compares most favorably with spectrum (D), and the detail in the 2,156 cm^{-1} to 2,220 cm^{-1} region is actually due to CO_2. Figure H-4 shows this spectral region at 0.25 cm^{-1}; it is seen that the detail in (D) is actually composed of groups of spectral lines, and therefore is not due to CO emissions.

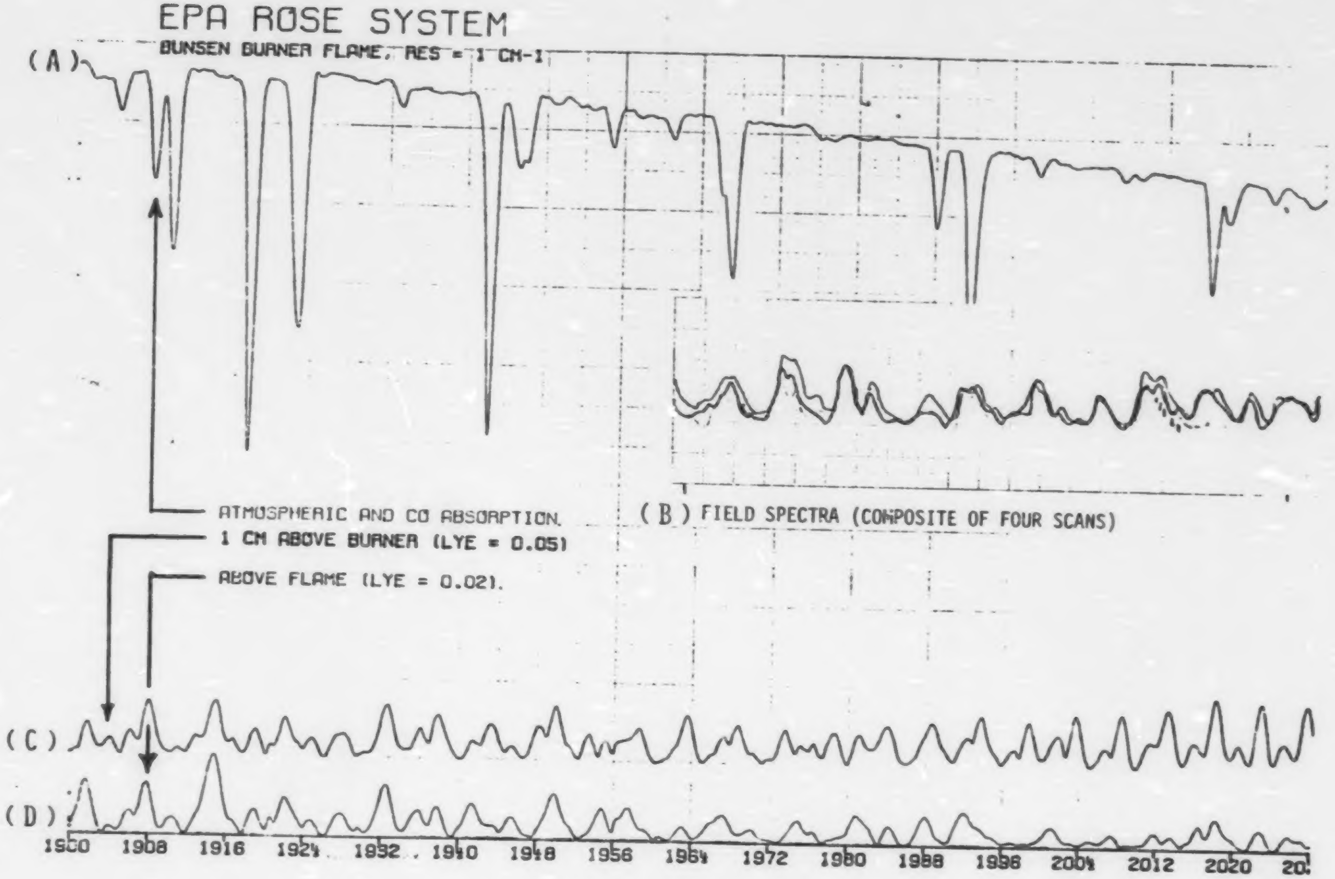

Figure H-3. Comparison of field spectra and laboratory spectra obtained with FTS System

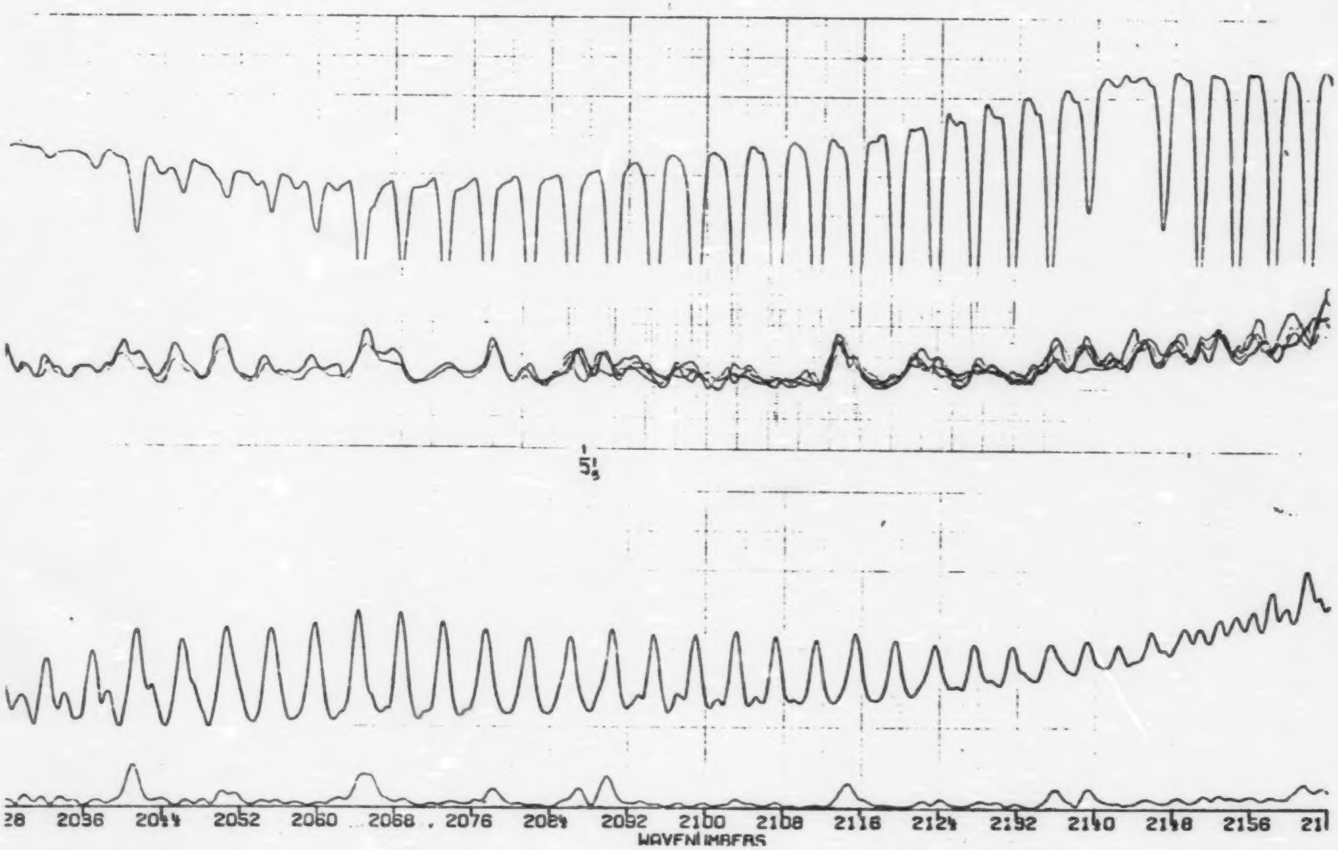

Figure H-3 (continued). Comparison of field spectra and laboratory spectra obtained with FTS System

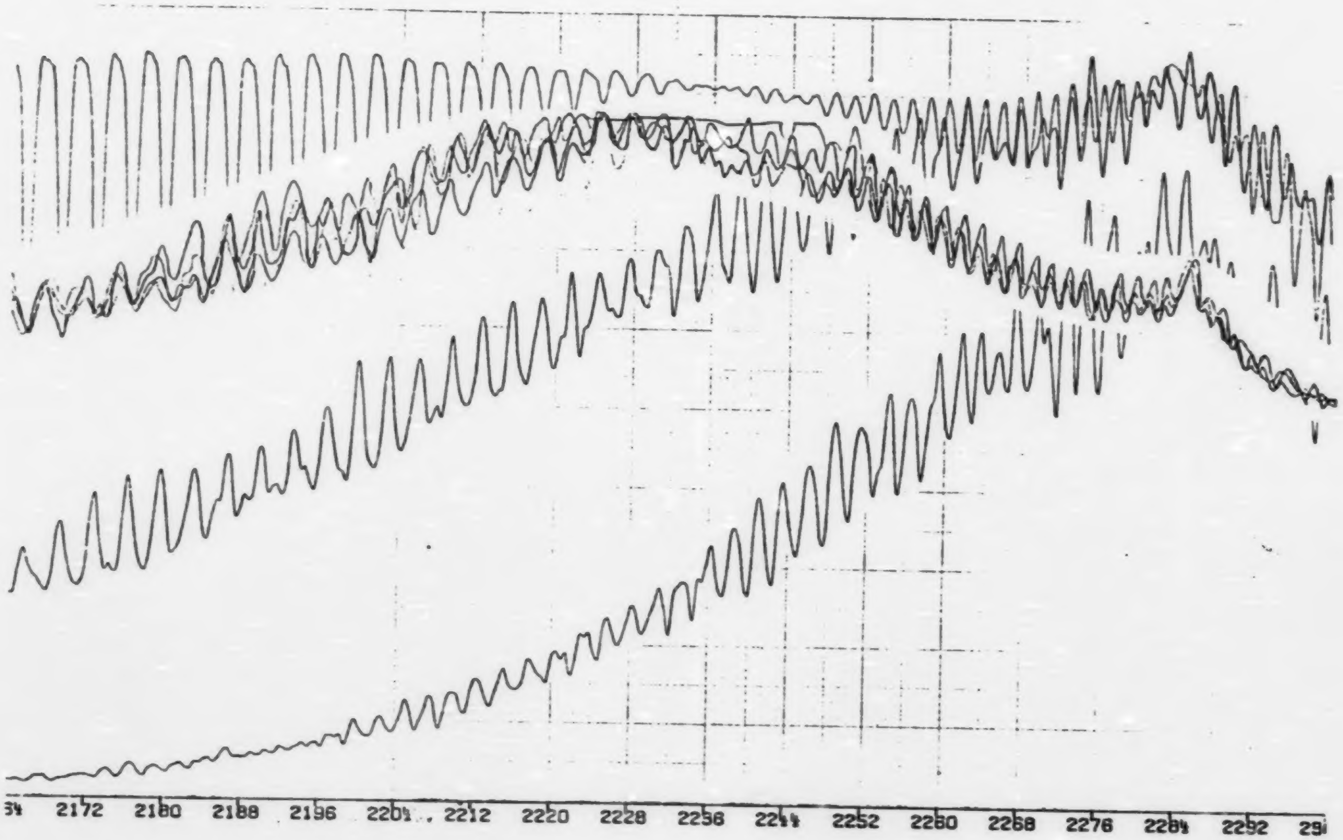

Figure H-3 (continued). Comparison of field spectra and laboratory spectra with FTS System

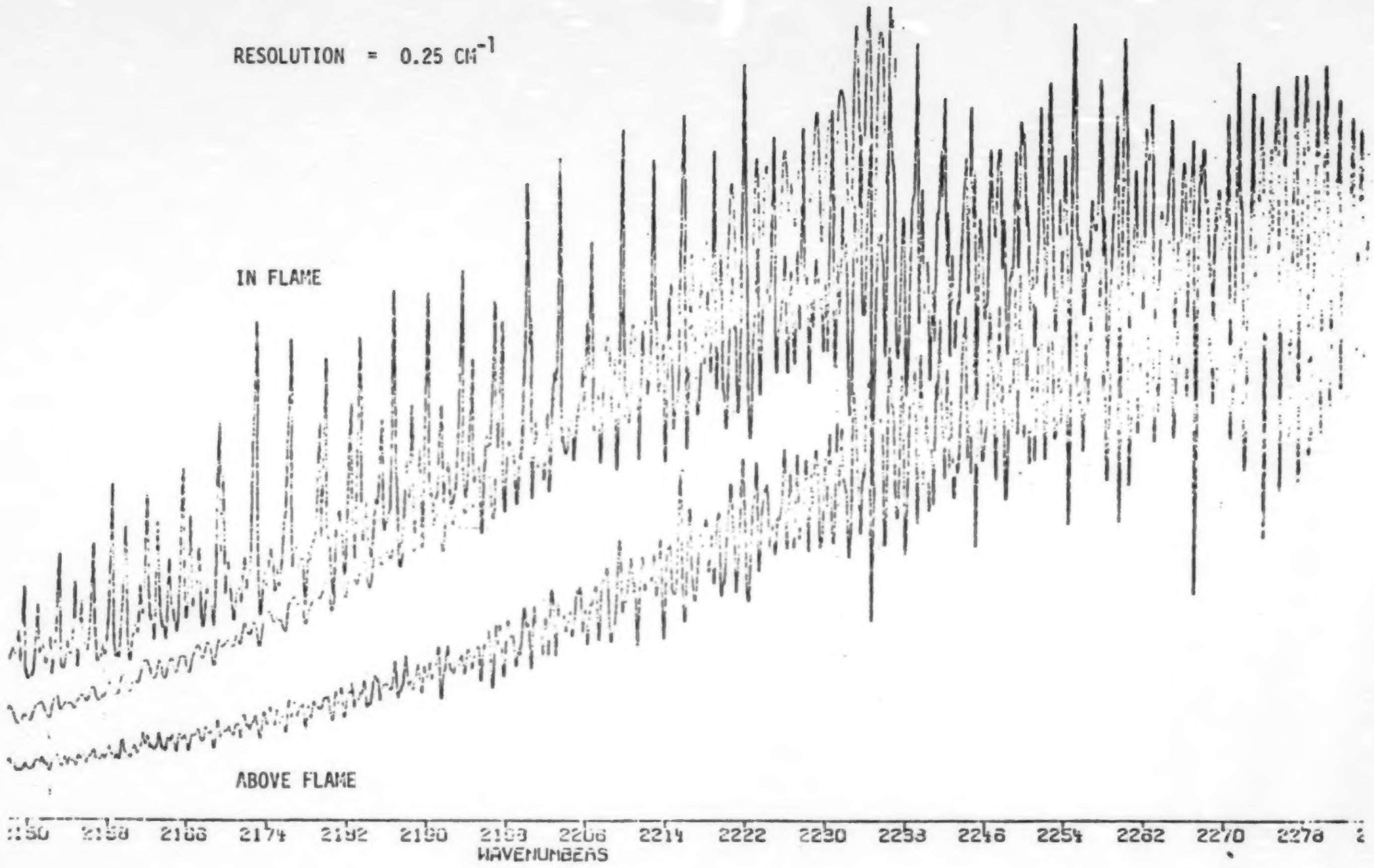

Figure H-4. Laboratory spectra at resolution of 0.25 cm^{-1}

The concentration reduction in the bunsen burner flame was determined from spectra shown in Figure H-5. Spectrum (A) shows the atmospheric absorption between the bunsen burner flame and the FTS dector; (B) and (C) are flame absorption spectra, and the lower spectrum is ambient temperature CO absorption. The CO reduction from (C) to (B) was calculated to be at least 25. This reduction, coupled with the factor of 100 determined as in the previous study[11] (flare off-gas spectra with respect to incorrectly identified CO lines) gives an overall reduction of at least 2,500 in CO concentration.

3. SUMMARY OF RESULTS

The bunsen burner studies showed that the field spectra were comparable to bunsen burner spectra obtained from just above the visible portion of the flame, and that the CO content was considerably lower than those calculated previously.[11] The previous calculation was incorrect because spectral lines due to CO_2 emissions were incorrectly interpreted as being due to CO. The bunsen burner spectra obtained with the FTS System conclusively identified the error. It was determined that the CO concentration in the flare off-gas was lower by at least a factor of 25 that the concentrations reported in the previous work. The present results indicate that the flare reduces the CO concentration by at least a factor of 2,500.

The concentration of CO measured in the main provess vent gas was 11% by volume. A reduction in concentration by a factor of 2,500 corresponds to a concentration of approximately 50 ppm in the flare off-gas. The CO control efficiency of the flare is therefore greater than 99.9%.

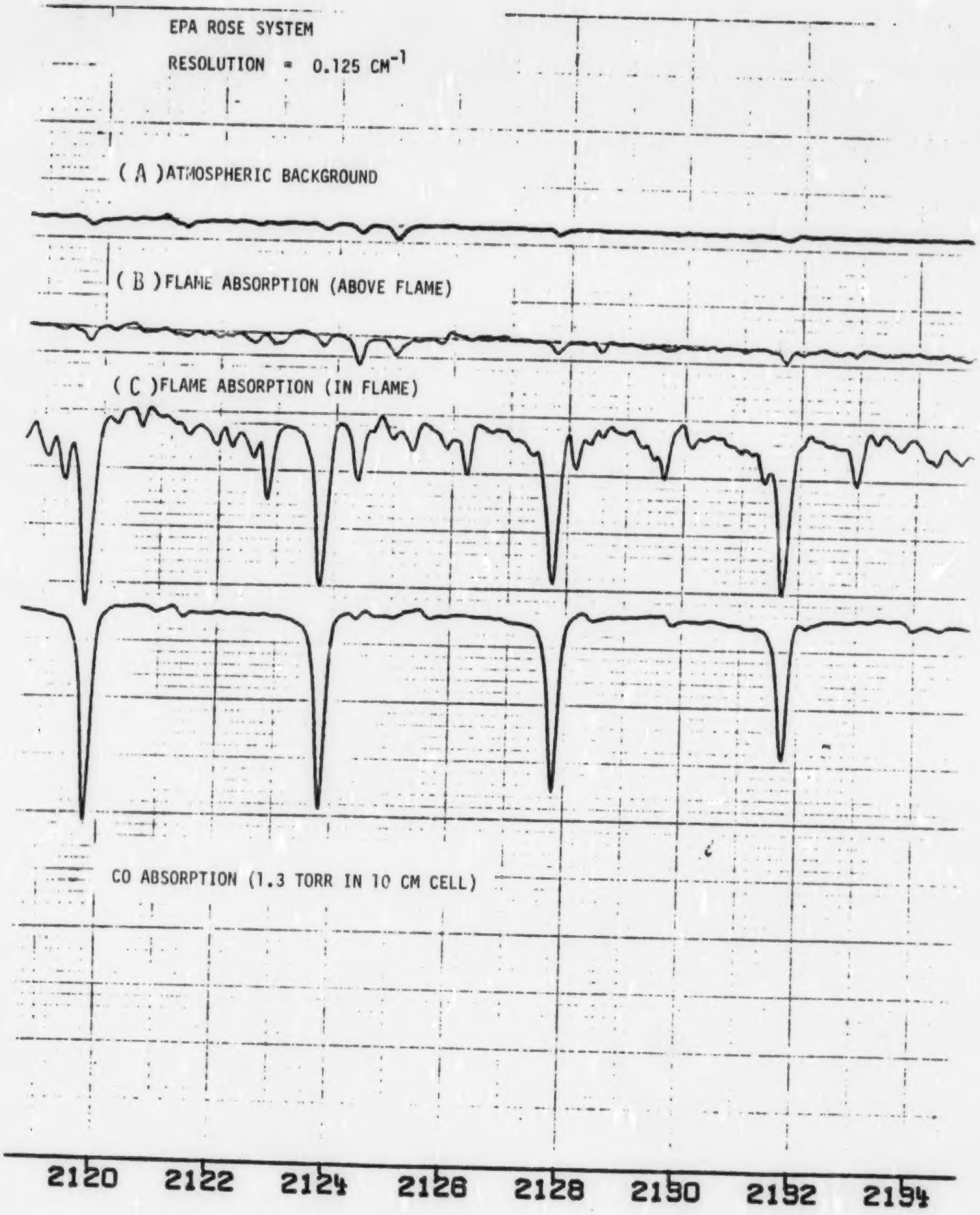

Figure H-5. Spectra used to determine reduction in CO concentrations

SECTION VIII

GLOSSARY OF TERMS

ATMOSPHERIC STABILITY CLASS - Class used to designate degree of turbulent mixing in the atmosphere.

CRITERIA POLLUTANT - Emission species for which an ambient air quality standard has been established.

EMISSION FACTOR - Weight of material emitted to the environment per unit weight of carbon black produced.

FEF CARBON BLACK - Fast extruding furnace grade black made by oil furnace process (see Table 2 for properties; see Tables 48 and 49 for applications).

GPF CARBON BLACK - General purpose furnace grade black made by oil furnace process (see Table 2 for properties; see Tables 48 and 49 for applications).

HAF CARBON BLACK - High abrasion furnace grade black made by oil furnace process (see Table 2 for properties; see Tables 48 and 49 for applications).

ISAF CARBON BLACK - Intermediate super abrasion furnace grade black made by oil furnace process (see Table 2 for properties; see Tables 48 and 49 for applications).

NONCRITERIA POLLUTANT - Emission species for which no ambient air quality standard has been established.

OIL FURNACE PROCESS - Continuous process for production of carbon black from a liquid hydrocarbon feedstock.

PELLETIZER - Machine which agglomerates raw carbon black into pellets for ease of handling and transporting.

PNEUMATIC SYSTEM - Pneumatic conveyor used to transport raw carbon black from product recovery area of plant to product treatment area of plant.

POLYCYCLIC ORGANIC MATERIAL (POM) - Organic compounds containing two or more benzene ring structures.

SAF CARBON BLACK - Super abrasion furnace grade black made by the oil furnace process (see Table 2 for properties; Tables 48 and 49 for applications).

STRUCTURE - The formation of chain-like aggregates of carbon black particles; it affects the rheology of carbon black-elastomer systems.

TANK OUTAGE - Distance from liquid surface to top of storage tank.

THERMAL PROCESS - Cyclical process for production of carbon black from natural gas.

VACUUM CLEANUP SYSTEM - Plant-wide vacuum system used to pick up loose carbon black.

SECTION IX

CONVERSION FACTORS AND METRIC PREFIXES[65]

CONVERSION FACTORS

To convert from	to	Multiply by
degree Celsius	degree Fahrenheit	$t^{\circ}_{F} = 1.8\ t^{\circ}_{C} + 32$
joule (J)	British thermal unit	9.479×10^{-4}
kelvin (K)	degree Celsius	$t^{\circ}_{C} = t^{\circ}_{K} - 273.15$
kilogram (kg)	pound-mass (lb mass avoirdupois)	2.204
kilogram (kg)	ton (short, 2000 lb mass	1.102×10^{-3}
kilogram/meter^3 (kg/m^3)	gram/cm^3	1.000×10^{-3}
kilogram/meter^3 (kg/m^3)	pound-mass/foot^3	6.243×10^{-3}
kilometer^2 (km^2)	mile^2	2.591
meter (m)	feet	3.281
meter (m)	mile	6.215×10^{-4}
meter^2 (m^2)	feet^2	1.076×10^{1}
meter^3 (m^3)	barrels (42 gal)	6.293
meter^3 (m^3)	feet^3	3.531×10^{1}
meter^3 (m^3)	gallon (U.S. liquid)	2.642×10^{2}
metric ton	pound-mass	2.205×10^{3}
ohm-meter (Ω-m)	ohm-centimeter	1.000×10^{2}
pascal (Pa)	inch of mercury (60°F)	2.961×10^{-4}
pascal (Pa)	pound-force/inch^2 (psi)	1.450×10^{-4}

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[65] Standard Metric Practice Guide. ASTM Designation E380-74, American Society for Testing and Materials, Philadelphia, Pennsylvania, 1974. 34 pp.

METRIC PREFIXES

Prefix	Symbol	Multiplication factor	Example
mega	M	10^6	1 MJ = 1 x 10^6 joules
kilo	k	10^3	1 kPa = 1 x 10^3 pascals
milli	m	10^{-3}	1 mg = 1 x 10^{-3} gram
micro	μ	10^{-6}	1 μm = 1 x 10^{-6} meter
nano	n	10^{-9}	1 nm = 1 x 10^{-9} meter

SECTION X

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